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State of Washington

Control of Toxic Chemicals in Puget Sound: Assessment of Selected Toxic Chemicals in the Puget Sound Basin, 2007-2011

Addendum No. 1:

Evaluation of Fate and Transport Mechanisms for Primary Releases of Copper, PCBs, and PBDEs

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Acronyms and Abbreviations

ADT	average daily traffic
ADVMT	average daily vehicle miles traveled
AWDT	average weekday traffic
BMPs	best management practices
cfs	cubic feet per second
COC(s)	contaminant(s) of concern
CSO	combined sewer overflow
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management System
PAHs	polycyclic aromatic hydrocarbons
PBDEs	polybrominated diphenyl ethers
PCBs	polychlorinated biphenyls
PRE	percent removal efficiency
PSTLA	Puget Sound Toxics Loading Analysis
SEATAC	Seattle-Tacoma International Airport
SPMDs	semi-permeable membrane devices
SR	State Route
TCLP	Toxicity Characteristic Leaching Protocol
TSS	total suspended solids
USGS	U.S. Geological Survey
VMT	vehicle miles traveled
WWTP	wastewater treatment plant

Abstract

Environmental releases of contaminants of concern were categorized according to similar pathways taken to Puget Sound, attenuation processes occurring along the pathway and management strategies that would control releases. Releases were first grouped into two major categories according to the extent to which the releases were initially constrained by physical infrastructures, and then by initial modes of release.

The primary contributions of the U.S. Geological Survey to the Puget Sound Toxics Loading Analyses are to: (1) propose a methodology for evaluating fate and transport mechanisms of transport for copper, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), and (2) conduct case studies of these three chemicals using proposed methodology. The case study on copper focused on releases from roofs and dust from brake pads and tires along the surface water pathway. The review of the literature suggests that the degree of attenuation of copper in urban basins is highly site specific and depends on such factors as how rainwater is routed from the gutters of buildings, the nature of roads (road gutters and shoulder types), the type and efficiency of stormwater infrastructures and the nature of stream riparian and hyporheic zones.

The estimated releases of total copper within the Mill and Thornton Creek basins were compared to the copper loadings discharging from the basins during 35 storm events. About 3% of the copper estimated to have been released in the Mill Creek basin was discharged by Mill Creek. Up to 7% of the copper estimated to have been released in the Thornton Creek basin was discharged by Thornton Creek. The difference in attenuation between these two basins is a result of differing geographies, riparian zones and stormwater infrastructures. These copper case studies emphasize that understanding the releases, partitioning and transport of copper in urban streams is basin specific and requires data more specific than land use/land cover.

PCBs and PBDEs in urban waters only recently have been analyzed at ambient concentrations of ng/L and pg/L levels, respectively. The partitioning between dissolved and particulate phases have been determined in a few research projects. A better understanding of attenuation processes will occur when concentrations are measured at ambient levels in urban waters as part of longitudinal studies.

Introduction

Bioaccumulation of toxic chemicals in freshwater and marine food webs in the Puget Sound basin continues to be a concern for environmental managers and the general public. With renewed interest, Washington State Department of Ecology (Ecology) began a phased, coordinated Puget Sound Toxics Loading Analysis (PSTLA) in 2006 to understand the sources and management options for controlling the loadings of a number of toxic chemicals to Puget Sound (Ecology, 2011a). In Phase 1, rough estimates of loading for a number of contaminants of concern (COC) were developed. In Phase 2, more detailed analyses of existing data were undertaken to improve the loadings by surface runoff, especially runoff from roadways, direct spills to Puget Sound, discharges from municipal and industrial wastewater treatment plants and combined sewer overflows.

In Phase 3, new data were collected to better quantify the loadings of specific COCs from specific pathways contaminants follow to Puget Sound (e.g., surface runoff and atmospheric deposition). In addition, new data on the exchanges of fresh and marine waters between the Sound and the Pacific Ocean were collected.

One aspect of Phase 3 of the PSTLA is to identify the sources of selected COCs released to the environment, to identify the pathways in which selected COCs are transported to Puget Sound, and to examine attenuation of COCs along these pathways in case studies using existing data. Ecology limited the COCs to several metals (arsenic, cadmium, copper, lead, mercury and zinc), several synthetic industrial organics (polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxin and furans, phthalates, nonylphenol), one pesticide (Triclopyr), polyaromatic hydrocarbons (PAHs), and total petroleum hydrocarbons.

Ecology (2011b) estimated the initial releases of each of the COCs to Puget Sound from a wide range of primary sources. In this system of source identification, road runoff is not a source, but a part of the overall pathway of surface runoff. Thus, the initial releases of COCs to road runoff are the many primary sources used in the vicinity of roads, such as oil drippings from cars, brake pad dusts, leaching from guard rails and roadside application of pesticides.

This addendum evaluates attenuation processes, based on literature research, after COCs are released to the Puget Sound basin. The role of the U.S. Geological Survey (USGS) in this study was to propose methodologies for evaluating transport and attenuation from these primary sources along pathways to Puget Sound. To test this conceptual model, case studies for copper, PCBs and PBDEs were conducted in large urban basins in Puget Sound basin. The availability of attenuation literature and environmental data in the Puget Sound basin dictated the relative complexity of the case studies.

Conceptual Model

In the initial step of the conceptual model, the primary sources of COC identified by Ecology (2011b) are grouped by similar modes of initial release. Within the scope of this study, it is unrealistic to identify and quantify the attenuation processes that affect each of the primary sources. Primary sources of COCs within each mode are initially released to the environment in a similar media (e.g., water), released by similar physical processes (e.g., abrasion), follow the same pathway to Puget Sound, are controlled by similar attenuation processes and can be controlled by similar management strategies.

Pathways previously discussed in the PSTLA include surface runoff, combined sewer overflows, discharges from municipal and industrial wastewater treatment plants, and atmospheric transport. Direct releases to the marine waters to Puget Sound and oceanic exchange have also been identified as pathways, but are not discussed in this addendum because no attenuation occurs. Although it has been mentioned in a number of contaminant studies for Puget Sound, groundwater flow has been examined in few investigations as part of Ecology's toxics control program (Pitz, 2011) and is added as a pathway considered in this document. In this conceptual model, the transport and attenuation of the primary sources will be examined along the pathways of 1) surface runoff, 2) groundwater, 3) combined sewer overflows, 4) discharges from municipal and industrial wastewater treatment plants, and 5) atmospheric transport.

Given the context of loadings of COCs, attenuation to Puget Sound along these five pathways is defined in this addendum as: "*the ability to remove COCs from fluid flow by various mechanisms such as settling, adsorption, biological uptake within the transit time through the water or air body of interest leading to transfer of elements or compounds to temporary or permanent reservoirs or leading to the decomposition of organic compounds*" (adapted from wordIQ.com, 2010). Under certain circumstances, attenuation processes are reversed, which lead to temporary reservoirs over times scales greater than transit times. Examples of temporary reservoirs include uptake of COCs by seasonal vegetation, COCs in snow pack, particle trapping by macrophytes during low flows, settling of particles in temporary deposition zones in streams and lakes, and COCs in groundwater supplying base flows as a result of the delayed effects of recharge during storm events.

The spatial domain of the conceptual model needs to be defined, especially in the vertical dimension, in order to categorize the releases from primary sources in a consistent manner. The horizontal domain of the loadings model has been set as the Puget Sound Action Areas by the Puget Sound Partnership (2010). In the vertical dimension, the Puget Sound airshed is included in the model domain. With this definition of the model domain, atmospheric transport of COCs from the west over the Pacific Ocean, and emissions to the airshed within the model domain, are considered primary sources. Atmospheric transport within the model is an internal pathway and can be examined by measuring the atmospheric deposition of contaminants.

Modes of Initial Release of Primary Sources

Thirteen modes of initial release are identified and include groupings of sources, such as mobile sources, buildings and grounds, household products discharged to sanitary sewers and land application as a liquid. The 110 primary sources (Appendix A, Tables A1 and A2) described by Ecology (2011b) are grouped in these 13 modes based on similar pathways to Puget Sound, similar attenuation processes along the pathway, and similar management actions that would reduce the loadings of COCs to Puget Sound.

The 13 modes of initial release were further categorized according to the extent to which the releases within groups of primary sources were initially constrained by physical infrastructures, could be controlled by management actions, and the likelihood that COCs would initially be released to the basins of Puget Sound. Constrained releases from primary sources are constrained in buildings, pipes or stacks, are not likely to initially enter the surface runoff pathway, and have been traditionally controlled by point-source technologies. The seven grouping of initial modes of release for constrained releases are:

- Water conveyance
- Household products
- Industrial wastewater
- Commercial wastewater
- Abrasion and leaching of household products
- Volatilization of household products
- Industrial air emissions

Unconstrained releases from primary sources are initially released to the outdoor landscape of Puget Sound and are more likely to enter surface waters. The six grouping of initial modes of release for constrained releases are

- Buildings and grounds
- Mobile sources
- Land applications as liquids
- Land applications as solids
- Combustion from stationary sources and fugitive emissions
- Water applications

Constrained Releases

The primary pathways of constrained releases are limited to water discharges from municipal and industrial wastewater treatment plants and to atmospheric transport within the Puget Sound airshed (Table 1). Although the primary pathway of a specific mode of release may be constrained, site-specific conditions may lead to some releases that are unconstrained. For example, the majority of COCs released by water conveyance systems flow to wastewater treatment facilities; but COCs from houses served by septic systems enter the groundwater system or the surface water pathway in the case of failing septic systems.

COCs from water conveyance systems could enter the surface water pathway or a combined sewer system in the case of excessive lawn irrigation from a house bib, in which excess water will run onto the street. Primary releases transported by the industrial and municipal treatment pathway were previously investigated in the PSTLA and will not be examined in this report in detail.

Depending on basin, COCs in constrained releases may enter the surface water as combined sewer overflows in large urban areas serviced by combined sanitary/stormwater systems, as washoff of recycled municipal biosolids applied to land surfaces and as municipal discharges to rivers from smaller inland cities. COCs in wastewater discharged into rivers can settle into temporary or permanent sediment reservoirs in rivers or lakes. COCs in residential wastewater can enter the groundwater through the drain fields of septic systems. Organic COCs in household wastewater serviced by septic tanks can be decomposed in the septic system or during transit to surfaces waters through the vadose zone or groundwater aquifer.

Table 1. Pathways and reservoirs of constrained releases from primary sources.

	Pathway to Puget Sound					Reservoirs				
Modes of Release	**Surface Water**	**Ground-water**	**Combined sewer overflow**	**Waste water treatment plants**	**Atmo-spheric transport**	**Airshed**	**Soil reservoir**	**Sediment reservoir**	**Transfor-mation**	**Landfill**
Water conveyance[a]	√	√	√	X					√	
Household products[a]	√	√	√	X					√	√
Industrial wastewater[a]	√	√	√	X					√	
Commercial wastewater[a]	√	√	√	X					√	
Abrasion and leaching of household products[a,b]	√	√	√	X					√	√
Volatilization of household products[c]					X	√	√	√	√	
Industrial air emissions[d]					X	√	√	√	√	

[a]Sanitary contained infrastructure
[b]Garbage contained infrastructure
[c]Indoor air contained infrastructure
[d]Stacks contained infrastructure
X = Primary pathway and reservoir determined by site-specific conditions
X = Pathway and reservoir not determined by site-specific conditions
√ = Pathway and reservoir determined by site-specific conditions
√ = Pathway and reservoir not determined by site-specific conditions

Releases to air include volatilization of consumer products, residential heating systems, and industrial air emissions. Constrained sources also include all releases inside homes and commercial and industrial buildings. Indoor releases may be diffuse, but institutional and management actions similar to larger constrained sources to reduce releases and loadings to Puget Sound can be easily initiated.

The majority of COCs leaving indoor spaces through ventilation systems and open doors and windows probably originates during volatilization of consumer products. This atmospheric pathway is especially important for PBDEs from furniture and PCBs from indoor caulk of industrial structures built in the 1950s and 1960s. Elevated concentrations of COCs in indoor air are released to the Puget Sound airshed and enter the surface runoff pathway by internal cycling within the Puget Sound model domain by atmospheric deposition. Fate and attenuation of COCs from the Pacific Ocean atmospheric sources and releases from primary sources to the Puget Sound airshed through the atmospheric pathway can be assessed by modeling deposition of COCs within the model domain.

COCs released in buildings as solids generally are transported to landfills by general housekeeping practices. Abrasion of household products containing COCs can find their way to the landfill as household sweepings discarded in the trash, to groundwater or municipal discharges as wash water during mopping of floors, or to the airshed by fugitive emissions through doors and windows.

Unconstrained Releases

Unconstrained releases of COCs from primary sources initially enter the outdoor environment in a diffuse manner that is not easily controlled. Unconstrained releases were grouped into six categories (Table 2) based both on use of the primary sources and likely pathways to Puget Sound.

Table 2. Applicable pathways and sinks and reservoirs for unconstrained releases of contaminants

	Pathway to Puget Sound					Reservoirs				
Modes of Release	**Surface Water**	**Ground-water**	**Combined Sewer Overflow**	**Waste-water Plants**	**Atmo-spheric Transport**	**Airshed**	**Soil reservoir**	**Sediment Reservoir**	**Transfor-mation**	**Landfill**
Buildings and grounds	X	√	√	√	√	√	√	√	√	√
Mobile sources	X	√	√	√	√	√	√	√	√	√
Land applications as liquids	X	√	√	√	√	√	√	√	√	√
Land applications as solids	√	√	√	√	√	√	X	√	√	√
Combustion from stationary sources and fugitive emissions					X	√	√	√	√	√
Water applications	X							√		√

X = Primary pathway and reservoir determined by site-specific conditions

X = Pathway and reservoir not determined by site-specific conditions

√ = Pathway and reservoir determined by site-specific conditions

√ = Pathway and reservoir not determined by site-specific conditions

Buildings and Grounds

Sources of COCs released from the Building and Grounds category include all above-ground structures and outdoor home accessories that can leach, abrade, and volatilize. COCs in this category includes roof runoff that contains COCs in rainfall, in products from a variety of roof materials that are leached or abraded, in moss control products, sealants on residential and commercial buildings, paints and any plastic products that contain COCs used on or around the house.

The pathway followed by roof runoff to Puget Sound is site specific. Some roof runoff is transported directly to roads or stormwater systems. Chemical and physical processes affect the fate of COC as roof runoff flows over the roof, into the gutter, and down the downspout towards the conveyance system that will disperse the water away from the building. From the downspout, the water is conveyed to a variety of surfaces and structures. Roof runoff piped directly to a combined sewer-stormwater system (illegal in many jurisdictions in Puget Sound) flows to a wastewater treatment facility and does not enter the surface system, except in the event of a combined sewer overflow. Likewise, roof runoff piped to a sub-surface infiltration system (in areas of well drained soils) does not immediately enter the surface water system and COCs are likely attenuated to a great extent by adsorption and decomposition. The groundwater will eventually flow to a stream or directly to Puget Sound.

Roof runoff can be piped directly to a street or directed onto splash boards that direct the flow across the lawn or down the driveway to the street. Once on the street, the pathway of COCs to Puget Sound will be dictated by the type of stormwater system (separate or combined).

Abrasion and leaching of primary sources of COCs on the vertical sides of buildings also release COCs. Abrasion of outdoor caulk will likely accumulate in soils around the perimeter of institution buildings, in the same manner in which lead is found in soil around older houses, or be transported to the stormwater system where pavement abuts the building. The erosion of soil around institutional buildings containing PCB-containing caulk and at PCB spill sites can transport PCBs to the stormwater system during heavy rainfall.

Roads and Mobile Sources

The category of roads and mobile sources includes abrasion of roads, leaching from highway signs and guard rails, right of way maintenance, drippings of oil from vehicles, leaching of plastics parts, and wear of brakes and tires. For the COCs in particulate form and those leached into the aqueous phase during rain events, the pathway to Puget Sound is site specific. If the area of interest is served by a combined stormwater/sanitary system, the COCs may be treated by wastewater treatment facilities, except during combined sewer overflows. Even in areas served by separate stormwater systems, the nature of the stormwater system will dictate the pathway. In systems in which stormwater flows through grassy ditches or other permeable structures, a significant fraction of the stormwater may infiltrate into the ground.

Land Application as a Liquid

As a result of spills, leaks and improper disposal, a number of oils and other fluids flow to the impervious and permeable surfaces. Examples include gasoline spills at stations and by tankers during transit, improper disposal of motor oil, and leakage of oils from capacitors and transformers. Fluids spilled on impervious surfaces will likely be efficiently transported to the stormdrain system. Depending on the properties of the fluid and COC, the COC may be degraded or volatilize before reaching the stormdrain.

Liquids flowing onto permeable surfaces are less efficiently transported to the stormdrain because of infiltration into and subsequent adsorption onto soils. For those COCs reaching the storm drain, the pathway will depend on whether the stormwater system is a separate system or combined with the sanitary sewer. In the case of spills, the COCs in absorbent textiles used to clean up the spill will be disposed of in the landfill.

Land Application as a Solid

For large-sized products in which the COC is an integral part of the product, physical or chemical processes must occur in order to release the COC from the product. PAHs can also be abraded in small particles, or low molecular weight PAHs can be leached by rainwater. These particulate or aqueous phase PAHs may be transported by surface water. In contrast, the granular forms of products used for residential or commercial lawn use can be transported as particles. The leaching of the COCs from these granules will more effectively transport the COCs to the stormwater system where they will be transported to Puget Sound by surface waters, through wastewater treatment plants or as a result of combined sewer overflows.

Combustion from Stationary Sources and Fugitive Emissions

COCs can be released into the airshed by trash and leaf burning, from fugitive emissions of gasoline from filling stations, and by volatilization of personal care products such as hair spray or nail polish. Solar heating can cause the PAHs in creosote railway ties or telephone poles to volatilize or decompose. These airborne COCs will be transported out of the Puget Sound airshed, be deposited directly on the surfaces of Puget Sound, or be deposited on land. Once deposited on land, the COCs can be sequestered by soils and be washed into surface waters. The residual material (ash) from combustion of a number of combustion products (ash) are usually scattered on the landscape or transported to landfills.

Water Applications

The intentional application of COCs directly to freshwater is very controlled by environmental laws and is limited to a few pesticides, such as Triclopyr. The direct application of these COCs means that the entire mass of the application enters the waterway and only chemical transformation and adsorption onto settling particles will reduce the loading of the COC to Puget Sound.

Recreational activities add the metal lead directly to surface water through the loss of fish weights and use of ammunition shot. Since the lead is incorporated into the weights and shots, the lead must be abraded or dissolved in order for the lead to be transported to Puget Sound. Since abrasion and dissolution are slow processes, these forms of lead can be considered a temporary reservoir which is likely to release lead for a long time.

Review of Transport, Fate and Attenuation of Copper in the Surface Waters

Ecology (2011b) indicate that the four major primary sources of copper released to the Puget Sound basin are domestic garden and lawn use of pesticides, domestic water conveyance (plumbing, fixture, pipe and solder), vehicle use (brake pads and tires), and roof runoff.

Copper released from water conveyance systems generally is transported to Puget Sound by the wastewater treatment pathway and does not substantially contribute to surface waters. The copper applied to gardens and lawns is likely to be incorporated into soils and vegetation. Little of the copper in landscaping pesticides washes off into surface water (Rice et al., 2001; Dietrich and Gallagher, 2002) if the pesticides are applied at recommended rates. The current state of the research on attenuation processes affecting copper from primary sources to urban streams is at the level of identifying the attenuation processes. The scope of the case study was further limited to storm events in urban streams based on the availability of concurrent flow and total copper concentrations at specific locations.

In the first attenuation section *From Buildings to Stormwater*, removal of copper between the time water falls on the roof until it enters the stormwater system or the road is examined. In the second section *From Vehicle/Roadway Sources to the Stormwater System*, copper is tracked from release from vehicles to the stormwater system. In the section, *From Stormwater to Urban Streams*, attenuation is assessed after road and roof runoff enters the stormwater system and stormwater flows through infrastructures implementing Best Management Practices (BMP) until the stormwater discharges to urban streams. Lastly, in the section *Urban Streams During Storm Events*, attenuation in in-line BMPs and within the stream channel are assessed.

Attenuation of Copper in Urban Streams

The speciation and partitioning between the dissolved and particulate phase in water along the various pathways strongly affects transport and attenuation processes. In addition to summarizing the literature on the partitioning and speciation of copper in urban waters, weathering processes that change the solution chemistry of a variety of urban waters will also be identified.

From Buildings to Roads or Stormwater Systems

Roof runoff is a primary source of copper from buildings (Ecology, 2011b). Baseline concentrations of copper in runoff from buildings and grounds are dictated by the quality of rain falling onto exterior building surfaces. Leaching and abrasion products from a variety of roof materials (patina, steel, tar, felt and asphalt shingles), flashing and moss control products increase copper concentrations in roof runoff above those of rain water.

The partitioning between dissolved and particulate phases and the solution chemistry (e.g., pH) of the roof runoff (Quek and Förester, 1993) will dictate the tendency of copper to be removed in stormwater conveyance systems. The percentage of copper in the dissolved phase was 66% and 77% for residential and commercial roof tops, respectively (Steuer et al., 1997 in Table A3). Chemical reaction with roofing, gutter and downspout materials can alter the solution chemistry of the roof runoff, which can change the extent of attenuation (Chang et al., 2004).

Like a number of COCs, copper concentrations in roof runoff seem to decrease with increasing rainfall (Zobrist et al., 2000). The type of roof material dictates both the amounts and chemical form of copper released (Quek and Forester, 1993). Patina roofs (weathered copper metal roofs that are generally green) released the greatest amount of copper, most of which is in the aqueous phase (Boulanger and Nikolaidis, 2003; Bertling and others, 2006). Little information is available on the concentration of copper in particles in roof runoff. Copper concentrations in particles from asphalt shingle roofs were 50-98 mg/kg (van Metre and Mahler, 2003), which were only slightly higher than copper concentrations in Puget Sound background soils (Table 3).

Table 3. Concentrations of copper, antimony, and total PCBs on particles in road dirt, street sweeping water, and sediment collected from catch basins.

Catch Basin	Location	N	Copper (mg/kg)	Antimony (mg/kg)	Total PCB (ug/kg)
Ames and Prych (1995)					
Soils	Western Washington	4	29 – 53	1.0 – 1.4	NA
van Metre and Mahler (2003)					
Roof Runoff (Asphalt shingle)	Austin, TX	6	50 - 98	NA	NA
Roof Runoff (Zn sheet)	Austin, TX	6	59 - 110	NA	NA
Legret and Pagotto (1999)					
Road Runoff	Nantes, France	43	20 - 260	NA	NA
This Study					
Road Runoff (Bridge)[a]	Seattle, Washington	3	297 - 1876	44 - 284	NA
Breault et al. (2005)					
Street Dirt	New Bedford, MA	--	133	NA	90 - 1700
Street Sweeping Solids (vacuum sweeper)	New Bedford, MA	--	43	<0.38	NA
Street Sweeping Solids (mechanical sweeper)	New Bedford, MA	--	56	0.68	NA
Jartun et al. (2008)					
Sediment collected in sediment traps	Bergen, Norway	63	16 - 6600	NA	<0.4 - 704
Karlsson and Viklander (2008)					
Sand and fines in catch basin in housing unit	Luleå, Sweden	5	24	NA	NA
Sand and fines in catch basin for road	Luleå, Sweden	5	53	NA	NA
King County (2005)					
Street Dirt (unswept streets)	West Seattle, WA	4	29.8-163	NA	19 - 20
Street Dirt (unswept streets)	Southwest Seattle, WA	4	25.4-466	NA	18 - 29
Street Dirt (unswept streets)	Duwamish Diagonal, Seattle, WA	4	55.3 - 92.3	NA	40 - 60
Street Dirt (swept streets)	Duwamish Diagonal, Seattle, WA	3	NA	NA	38 - 330
Street Sweeping Solids (regenerative-air)	West Seattle, WA	--	21.5 - 47.8	NA	<19, 1300
Street Sweeping Solids (regenerative-air)	Southwest Seattle, WA	--	23.2 - 75.5	NA	18 - 20
Street Sweeping Solids (regenerative-air)	Duwamish Diagonal, Seattle, WA	--	48.6 - 76.2	NA	230 - 910
Sediment from catch basin (unswept)	West Seattle, WA	--	41.4 - 80.7	NA	19 - 73
Sediment from catch basin (unswept)	Southwest Seattle, WA	--	43.8 - 198	NA	20 - 79
Sediment from catch basin (unswept)	Duwamish Diagonal, Seattle, WA	--	136 - 183	NA	34 - 150
Sediment from catch basin (swept)	Duwamish Diagonal, Seattle, WA	--	NA	NA	550 - 720
City of Seattle (2010)					
Sediment from catch basin	16th Ave S bridge (west), Seattle, WA	--	228	NA	264
Sediment from catch basin	16th Ave S SD, Seattle, WA	--	112	NA	220
Sediment from catch basin	2nd Ave S SD, Seattle, WA	5	80.4 - 131	NA	26 - 202
Sediment from catch basin	7th Ave S SD, Seattle, WA	4	48.8 -1 61	NA	20 - 251
Sediment from catch basin	Diagonal Ave S CSO/SD, Seattle, WA	9	38.4 - 203	NA	20 - 1110
Sediment from catch basin	S 96th St SD, Seattle, WA	2	26.2 -39.6	NA	1
Sediment from catch basin	S Brighton SD, Seattle, WA	2	186 - 230	NA	470 - 600
Sediment from catch basin	S River St SD, Seattle, WA	2	94.8 - 106	NA	54 - 56
Sediment from catch basin	SW Dakota SD/ditch, Seattle, WA	--	101	NA	133
Sediment from catch basin	SW Idaho SD, Seattle, WA	2	23.6 - 25.1	NA	20

[a]Concentrations calculated by dividing the difference of total and dissolved concentrations by the total suspended solids concentration
NA = Not analyzed

The attenuation of copper in roof runoff is highly site-specific (Figure 1) and depends on the route that roof runoff follows off the property: 1) directly to combined systems, 2) directly to stormwater drains, 3) directly to the road gutters, 4) across the lawn, 5) across driveways or 6) into on-site infiltration systems. Copper can be sequestered during its transport to roadways or stormwater systems by galvanic reactions with iron pipes, sequestering by concrete (Odnevall Wallinder et al., 2009), or trapped as particles by lawns or installed rain gardens (Dietz, 2007; Teemusk and Mander, 2007).

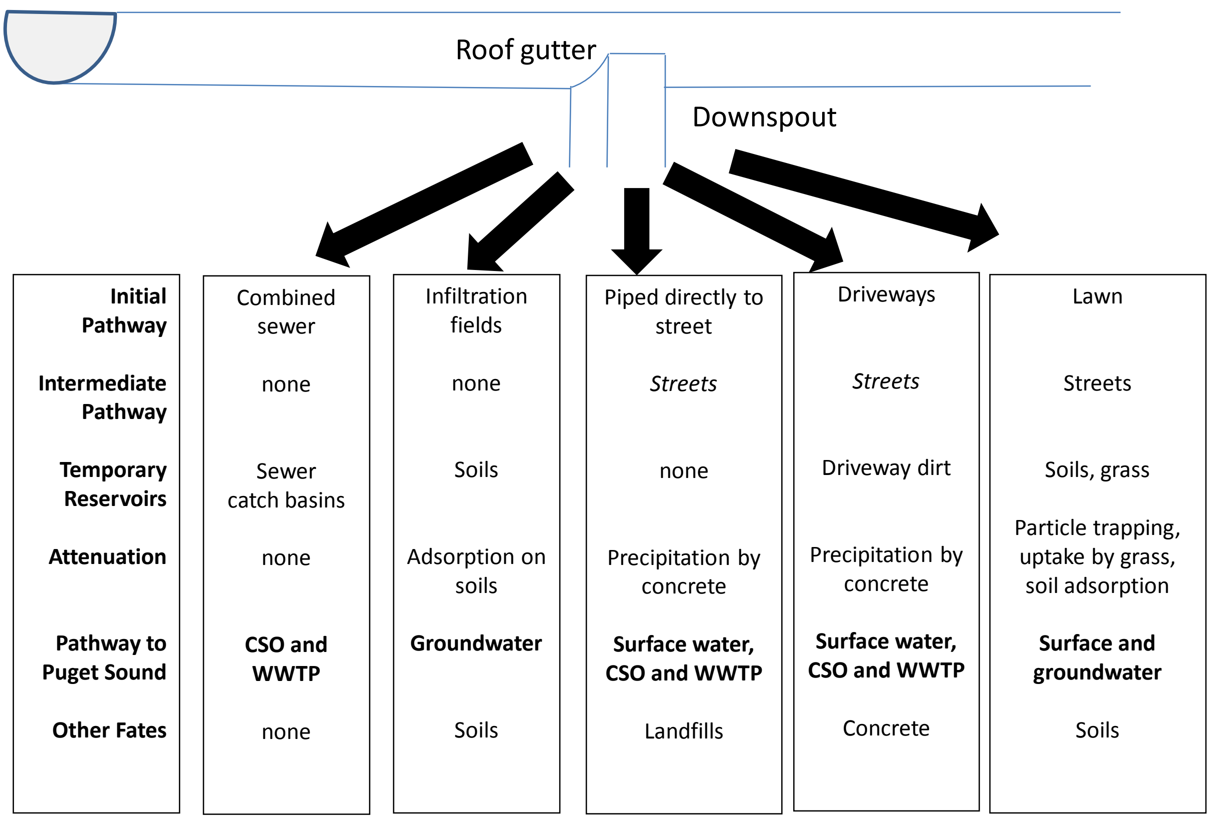

Figure 1. Pathways and fate of contaminants in roof runoff.

Partitioning, speciation and the exact route runoff takes off the property will dictate the loadings of copper from roof runoff entering urban streams. The route of roof runoff is site specific and is not only related to the municipal infrastructure, but also is dependent on how runoff is routed away from the building. When examining the transport of roof runoff in a specific geographical area, the extent to which roof runoff can bypass the stormwater system through combined stormwater-sewer systems and direct connection of downspouts to the sewer system should be examined. New technologies such as rain roofs and rain gardens may reduce copper loadings from buildings.

From Mobile/Roadway Sources to the Stormwater System

Copper in the street runoff originates from atmospheric deposition, releases from roofs and other building structures, leaching and abrasion of outdoor furniture, leaching from gardens and lawns, roadside litter, releases from mobile sources (brake and tire wear, leaching of contaminants off vehicles, and products of internal combustion) and abrasion, leaching of the road itself (especially road surfaces partially composed of recycled material) and road structures (guard rails and signs, etc.) and pesticide application for road maintenance. Folkeson et al. (2009) provide an overview of the sources and processes affecting the transport and transformation of contaminants from mobile sources.

For basins served by combined sewer-stormwater systems, road runoff (Figure 2) can flow to Puget Sound through combined sewer overflows and via wastewater treatment plants. Even in basins served by separate stormwater systems, some copper from mobile sources flows to wastewater treatment plants as effluent from commercial car wash facilities. The following section will focus on the following pathways of copper to Puget Sound: surface water, groundwater through infiltration of biofilters, atmospheric transport, and transfer to temporary reservoirs in soils and disposal in landfills. Folkeson et al. (2009) point out that water can also infiltrate into the groundwater through cracks and potholes in the road surface.

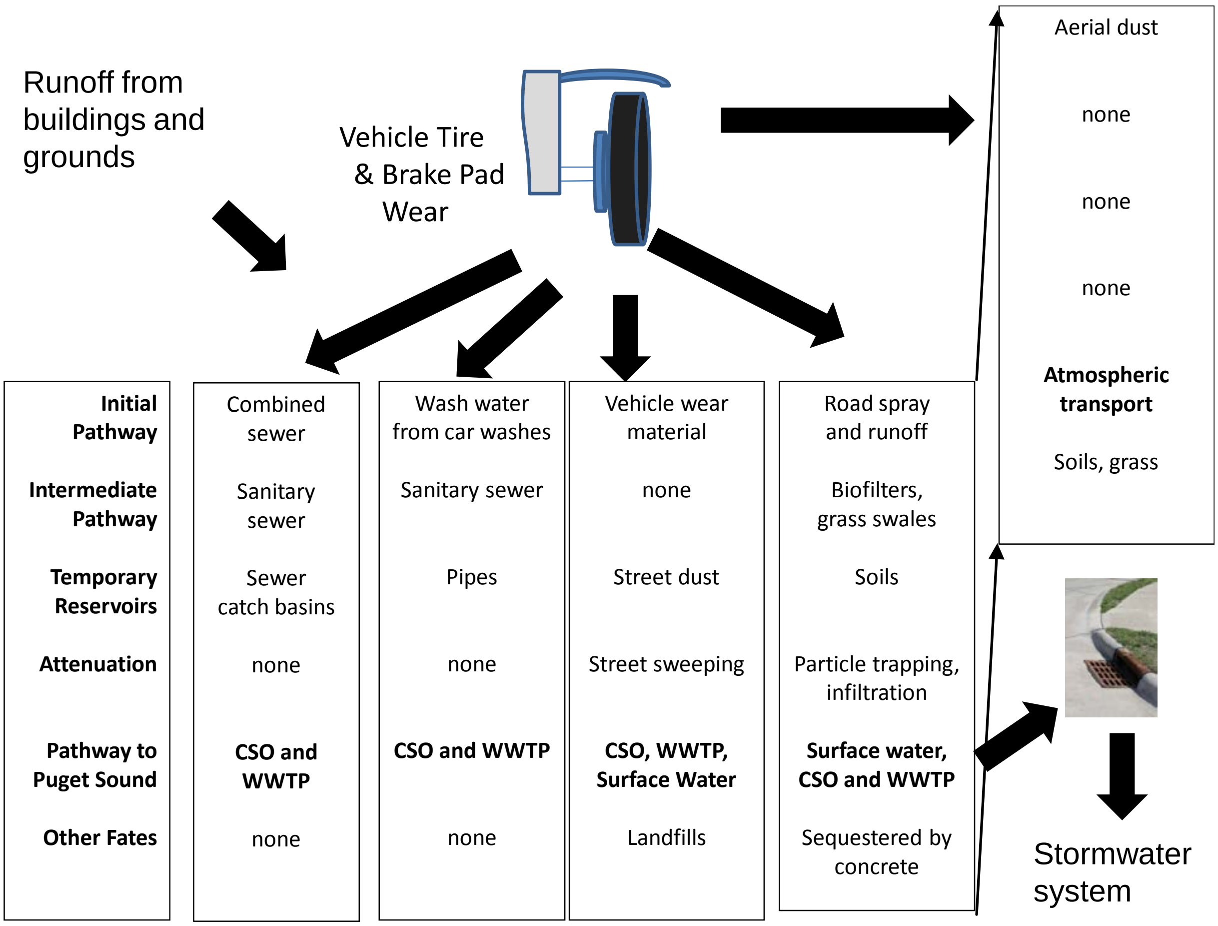

Figure 2. Pathways and fate of contaminants from mobile sources.

Partitioning and Speciation of Sources

Physical chemistry of brake pad dust

Research on speciation of metal sources associated with vehicles has been conducted on components of vehicles (brake assemblies and tires) under controlled laboratory conditions, within small segments of bridge roadway during field studies, and on urban stormwater. Release of copper from brake pads depends on traveling speed, deceleration level and frequency of stops. In controlled dynamometer tests, up to 45% of the mass of dust was released as particles less than 0.1 um (nanoparticles) (Garg et al., 2000).

Hur et al. (2004) examined the leaching characteristics of brake pad dust. About 60% of the copper was "leached" in only 0.5 hour and copper concentration of the test solution did not seem to reach equilibrium after the U.S. Environmental Protection Agency's standard 18-hour Toxicity Characteristic Leaching Protocol. This result was not necessarily surprising since nanoparticles would pass through a standard 0.2 um pore-size filter used in the protocol.

Copper concentrations in solutions in contact with the brake pad dust were similar to solubility of the mineral cuprite (Cu_2O). Similarity of copper concentrations with the solubility of cuprite suggest that copper in brake pads is partially oxidized during braking and copper in brake pad dust is soluble in natural waters at neutral pH. The pH of two urban streams evaluated in the case studies ranged between 6.4 and 8.0.

Bridge studies

In an effort to limit possible sources of COCs to only two sources (atmospheric deposition and roadway-related sources), two studies examined the loadings of COCs to confined areas of roadway on bridges. Legret and Pagotto (1999) reported the mean concentrations of unfiltered and filtered water generated from a length of motorway with an average daily traffic flow of 12,000 vehicles. For a mean total suspended solids (TSS) concentration of 71 mg/L, the percentage of total copper in the dissolved phase was 0.55% (Table A3).

Between April 2003 and January 2004, King County (2005) sampled three 9.1-m wide, 27.4-m long roadway panels on State Route 520 (SR-520) near Seattle over Lake Washington, WA, which the average daily traffic was 102,000 vehicles. Concentrations of COCs (conventional pollutants, metals, and a variety of organic compounds) were measured in unfiltered and/or filtered water. During three storms with antecedent dry periods between 1 and 15 days, total event rainfall ranged between 0.58 and 1.07 cm (Table 4).

The copper concentrations in the two events with antecedent dry periods of 1-2 days were different from those of the one event with an antecedent dry period of 15 days. For the two events with short antecedent dry periods, the mean TSS concentrations were 49.1 and 126.2 mg/L and 43% of the total copper was in the dissolved phase. In contrast, the TSS concentration of the one 15-day antecedent dry period was 6 mg/L and 82% of the total copper was in the dissolved phase. If one assumes that the concentration collected by the auto-sampler represents the total flow of the event (rainfall height times panel area), the release of copper was 0.03 mg/vehicle mile traveled (VMT) for the two short antecedent dry periods and 0.003 mg/VMT for the longer antecedent dry period.

Concentrations of metals in the particulate phase can be calculated indirectly from the difference between concentrations in unfiltered and filtered water. Particulate metal concentrations (in ug/L) were then divided by the TSS concentration (mg/L) to yield concentrations of copper (Cu) and antimony (Sb) on the SR-520 bridge particles (ug/mg), which can be converted to the commonly used concentration units:

Concentration of the particles (ug/mg) = Particulate Concentration (ug/L)/ TSS (mg/L) (eq. 1)

Table 4. Copper and antimony data from the State Route 520 study used to calculate unit vehicle release.

April 8, 2003: 0.19 days sampling; 0.32 in. rainfall, 1 day antecedent period, 1657-L event										
		Unfiltered water Sb:Cu=0.21 0.03mg Cu/vm		Aqueous Phase Sb:Cu=0.25		Percentage Dissolved			Particulate Phase Sb:Cu=0.17 maximum mass fraction of 0.18	
Constituent	**Unit**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Unit**	**Mean**	**SD**
TSS	mg/L	49.1	6.8	--	--	--	--	--		
pH	--	--	--	7.16	0.04	--	--	--	--	--
DOC	mg/L	--	--	23.3	3.1	--	--	--	--	--
Antimony, Sb	ug/L	7.8	0.3	4	0.3	52	4.8	mg/kg	75	2.1
Copper, Cu	ug/L	38	2	16.3	1.2	43	3.7	mg/kg	446	35.4
October 6, 2003: 0.08 day sampling, 0.23 in rainfall, 15 day antecedent period, 1210-L event										
		Unfiltered water Sb:Cu=0.11 0.003mg Cu/vm		Aqueous Phase Sb:Cu=0.11		Percentage Dissolved			Particulate Phase Sb:Cu=0.15 maximum mass fraction of 0.74	
Constituent	**Unit**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Unit**	**Mean**	**SD**
TSS	mg/L	6	1.2	--	--	--	--	--		
pH	--	--	--	7.08	0.08	--	--	--	--	--
DOC	mg/L	--	--	25.8	1.8	--	--	--	--	--
Antimony, Sb	ug/L	7.2	0.3	5.5	0.4	76	6.2	mg/kg	284	58.8
Copper, Cu	ug/L	64	12	53.4	13.6	82	6.2	mg/kg	1876	589.3
January 14, 2004: 0.42 days sampling, 2 day antecedent period, 1912-L event										
		Unfiltered water Sb:Cu=0.17 0.03mg Cu/vm		Aqueous Phase Sb:Cu=0.21		Percentage Dissolved			Particulate Phase Sb:Cu=0.15 maximum mass fraction of 0.12	
Constituent	**Unit**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Unit**	**Mean**	**SD**
TSS	mg/L	126.2	33.7	--	--	--	--	--		
pH	--	--	--	7.54	0.06	--	--	--	--	--
DOC	mg/L	--	--	38	7.5	--	--	--	--	--
Antimony, Sb	ug/L	11.3	1.1	5.8	0.2	51	6.5	mg/kg	44	2.3
Copper, Cu	ug/L	65	10	27	1.8	43	7.7	mg/kg	297	9.7

SD=Standard deviation

vm=Vehicle mile

Ecology (2011b) calculated that the median copper concentration of vehicle wear particles from brake pads and tires was 2,545 mg/kg. This concentration of vehicle wear particles can be used to estimate the maximum mass fraction of copper from vehicle wear (brake pad dust and tires) in the solids collected in the SR-520 bridge stormwater.

$$\text{Maximum mass fraction of vehicle wear particles} = \frac{\text{Concentration on the stormwater particles (mg/kg)}}{\text{Median vehicle wear particles concentration (mg/kg)}} \quad \text{(eq. 2)}$$

During the short antecedent dry period, between 11 and 18% of the solids in SR-520 stormwater particles were vehicle wear material. During the long antecedent drier period, vehicle wear material contributed up to 74% of the mass of the solids in SR-520 stormwater.

The majority of antimony in road dust may be contributed to brake pad dust because antimony is used as a lubricant in brake pads (von Uexküll et al., 2005). The ratio of antimony:copper concentrations of particles of the nine individual samples collected during the SR-520 study fell within a very narrow range of 0.14 to 0.18 (Table 4). This observation suggests that the antimony:copper ratio could be used as an indicator of brake pad dust.

Road studies

Of the few studies that examined partitioning in street and urban runoff (Table A3), only Bannerman et al., (1993) examined partitioning in a variety of pavements along the pathway of releases from roofs and vehicle wear material within the same basin. About 53% of the total copper flowing from residential driveways was in the dissolved form.

Total copper concentrations in storm water in feeder streets (residential streets) were higher than from residential driveway mainly as a resulted of increased particulate copper and TSS concentrations. The increase in particulate copper from driveways to feeder streets decreased the percentage of total copper in the dissolved form to 39%. The percentage of total copper in storm water from residential collector (arterials) that was in the dissolved phases was 43%. The percentage of total copper in storm water from commercial arterials (43%) was similar to that of residential areas. Both TSS and total copper in arterials in industrial areas were higher than arterials in residential and commercial areas; and only 16% of the total copper in industrial stormwater was in the dissolved phase.

Transport, Disposal and Attenuation

Physical dispersion of dust by vehicle tires transports particles to vegetation in the roadside right of way. Since Garg et al. (2000) showed that between 35% and 50% of the mass of brake pad mass loss was emitted as airborne particles, with a significant amount of released copper being exported away from the road. Some of the airborne particles may be transported out of the basin. On city arterials, the transport of dust off the road will be less for guttered streets compared to roads with gravel shoulders because of the height of the gutter.

If grassy strips are present between the edge of the road and separate stormwater conveyance system, the grassy strip may trap contaminants on particles and lead to limited infiltration of the water. However, the physical trapping of particles does not destroy metals and a reservoir of metals will accumulate in these grassy strips and other roadside vegetation that could lead to a slow release of the contaminant in the future.

Little research has been conducted on the environmental fate of copper in brake pad dust under natural conditions. Both the kinetics and equilibrium release of copper from brake pad dust into the dissolved phase is highly dependent on pH and solution chemistry (Hur et al., 2004). While 60% of the copper in brake pad dust is released in Synthetic Precipitation Leaching Solution at pH 5, less than 5% of copper is released to the aqueous phase at pH 7. The percentage of copper from brake pad dust that will be released into stormwater in the dissolved phase depends on the solution chemistry, mainly pH, and concentrations of compounds that complex copper.

Street Sweeping

Street sweeping and catch basin cleanout programs are proactive procedures that will permanently prevent COCs from entering urban streams. Selbig and Bannerman (2007) examined the efficiency of dirt removal and found that yield of dirt from the street was reduced by an average of 76%, 63%, and 20% when swept by the regenerative-air, vacuum-assist, and high-frequency broom sweepers, respectively. However, they found no statistically significant difference in the concentrations of total and dissolved copper in the stormwater. They suggest that this discrepancy between high dirt removal and no improvement in the water quality of stormwater can be explained if street sweeping increased the mechanical availability of fine particles to be transported to the gutter during storms.

Breault et al. (2005) examined the dirt accumulation in streets and concentrations of metals in five different size fractions of street solids including street dirt and waste captured by mechanical and vacuum sweepers (Table 3). From these data, the sweeping removal efficiencies of the street dirt were calculated for the five size fractions. The concentrations of copper in the street dirt varied from 51 mg/kg in gravel to 560 mg/kg in the silt/clay fractions (< 63 um). The majority of the mass of most metals resided in the coarse sand fractions, and the weighted average copper concentration of street dirt was 133 mg/kg. The efficiencies of mechanical sweeps decreased dramatically with particle size less than 250 µm and the efficiency of the vacuum sweepers varied dramatically between experiments.

The Seattle Street Sweeping Pilot Study (Seattle Public Utilities and Herrera Environmental Consultants, 2009) was designed to quantify the amounts of dirt and COCs 1) remaining in the street after sweeping, 2) the amounts removed by street sweeping, 3) the amounts accumulating in catch basins, and 4) the amounts discharged to urban receiving waters. The primary goal of the study was to improve water quality in receiving waters through improved efficiencies of street sweeping, but it was hoped that improved street sweeping would reduce the frequency and costs of Seattle's program of cleaning out catch basins. Street dust was vacuumed at paired areas which were swept and not swept (control) in residential West and Southeast Seattle on a monthly basis from July 2006 to June 2007, and the industrial Duwamish Diagonal from December 2006 to June 2007.

The amounts of dirt present in the streets (dirt yield) of two residential areas, West and Southeast Seattle, were on the high end of the national range. Differences in dirt yield between monthly sampling events were used to calculate dirt accumulation rates and to determine efficiencies of sweeping as measured by the relation between the mass picked up by sweepers versus what remained on the street.

For the two residential areas, street sweeping reduced the amount of dirt present in the street by 74 and 90% for West and Southeast Seattle, respectively, while the reduction in the industrial Duwamish Diagonal was 48%. Even though a significant amount of solids were removed by street sweeping, no significant difference in the accumulation of dirt in catch basins was observed. The average accumulation of dirt in catchment basins ranged from 35 to 70 grams per square meter of road surface per year. This accumulation is equivalent to average yields of 3.4 kg/curb km/day (12 pounds/curb mile/day) in the residential areas and 4.8 kg/curb km/day (17 pounds/curb mile/day) in the industrial Duwamish Diagonal.

Three monthly samples of street dirt, sweeper waste and sediment from catchment basins were composited into seasonal samples and analyzed for physical characteristics, metals, petroleum hydrocarbons, phthalates, PAHs and PCBs. Similar to Breault et al. (2005), sweeper waste contained a higher percentage of coarser material (>250 µm) than street dirt.

During the first 3 months of the study (July to September 2006), little or no rain fell on the study area. This condition allowed the comparison of the accumulation of total copper in unswept areas to the estimated release of total copper from vehicles. In West Seattle, less than 2% of the total copper estimated to have been released by vehicles accumulated in streets. This finding is consistent with the State Route 520 Bridge Study. In contrast, between 52 and 162% of the total copper estimated to have been released by vehicles accumulated in streets of Southwest Seattle. The copper concentrations of in street dust in this residential area were low (~100 mg/kg) compared to brake pad dust and tire wear material (2,545 mg/kg). This observation suggests that brake pad dust did not constitute a major component of the street sweepings in this area.

These values represent the maximum percentage of brake pad dust and tire particles that could have accumulated in roads and contribute to stormwater because 1) the dirt accumulation for August and September 2006 is an overestimate of average dirt accumulation because dirt in cracks was scrapped before sampling for these two months only, and 2) contribution of copper from the majority of dirt not associated with vehicles found on the street. It likely that the higher accumulation of copper in Southwest streets originated from sources other than brake pad dust, perhaps transfer of copper off lawn from domestic use of lawn and garden pesticides.

Without additional data and statistical analyses of the chemical composition that would provide information on the nature of the street particles whether by stormwater or street sampling, the discrepancy in the results from West and Southwest cannot be resolved. Using additional constituents such as aluminum (from natural clays), antimony (brake pads), zinc (tires) and other constituents, the contribution of brake pad dust, tire debris, erosional dirt, and roof particles to the mass of street dirt that would contribute COCs to the stormwater could be ascertained. The recent advances in analytical chemistry of metal isotope have also been applied to investigating the sources of copper and zinc in Lake Ballinger (Thapalia et al., 2010) and could be applied to understanding the sources of copper in solids in road runoff.

Car Washes

The wash water from cleaning copper-containing dirt off hubcaps and brake assemblies at commercial car washes enters either separate sanitary sewer or combined sewer systems. For basins with separated storm and sewer systems, effluent from commercial car washes is the primary means by which copper released from vehicles enters wastewater treatment systems. Elevated total copper concentrations were measured in commercial car wash effluents in Stockholm, Sweden (203 ug/L; Sörme and Lagerkvist, 2002) and in residential car wash effluents in Federal Way, Washington, USA (mean: 532 ug/L, range: 150 to 830 ug/L; Smith and Shilley, 2009). If an average volume of 300 L is used for each commercial car wash (cited in Sörme and Lagerkvist, 2002), then 61 mg of copper is transferred to wastewater treatment facilities for each car washed in a commercial facility.

Most residential car washing is performed on driveways and other impervious surfaces, which directly transfers copper to stormwater systems. Copper released from vehicles during residential car washing on side yards and gravel areas will be retained in soils or infiltrate into groundwater (Smith and Shilley, 2009). As a first approximation, the transfer rate of copper to wastewater treatment facilities for a basin could be calculated based on the frequency of use of commercial car washes within the basin.

Biofilters

Here we refer to biofilters as grass strips, grass swales, vegetated infiltration areas where road runoff can be treated before entering the storm system. For non-guttered streets, strips of grass between the gravel edge of road and the road-side ditches that carry storm water may retain dissolved and particulate copper. A search of the International Storm Water BMP Database (2010) for paired inlet/outlet data for biofilters was conducted to determine removal efficiencies for total and dissolved copper for grass strips and grass swales. For sets of paired inlet and outlet concentrations, the percent removal efficiency (PRE) for copper was calculated as follows:

$$\text{Percent Removal Efficiency (PRE)} = 100 * (1 - [\text{Outlet copper}/\text{Input copper}]) \qquad \text{(eq. 3)}$$

where copper is the total or dissolved concentration reported from the study. In many BMP studies, higher percent removal efficiencies are achieved with increasingly higher inlet concentrations (e.g., see Hossain et al., 2005). This is due to the concept of an irreducible concentration. In other words, if the inlet concentration of a pollutant is very low, it will be hard to reduce it further through a BMP. The median, minimum and maximum removal efficiencies for paired samples of grassy strips, grassy swales, detention ponds and retention ponds are summarized in Table 5 and details within each system are listed in Tables A4 and A5. Negative removals indicate that the outlet concentration was higher than the inlet concentration.

Table 5. Summary of percent removal efficiencies of total and dissolved copper by a variety of best management practices (BMPs).

BMP	Percent Removal of Total Copper: Systems	Events	System Statistics: Median	Min.	Max.	Event Statistics: Min.	Max.	Percent Removal of Dissolved Copper: Systems	Events	System Statistics: Median	Min.	Max.	Event Statistics: Min.	Max.
Grassy strip	12	219	53	5	87	-2700	97	12	203	24	-32	84	-253	98
Grassy swale	6	54	38	0	62	-129	86	5	40	5	-3	58	-56	63
Detention pond (dry)	3	61	11	-4	61	-159	93	3	54	0	-9	17	-558	93
Retention pond (wet) - Surface pond with a permanent pool	8	138	42	0	72	-400	97	3	48	18	16	20	-200	71
Vaults (wet) - Underground vault or pipe	3	21	30	-210	73	-210	95	3	26	22	-29	42	-125	94

The median PRE of total copper for 12 studies of grassy strips ranged from +5% to +87% with an overall median PRE across all sites of +53%. In 10 of the 12 studies, zero or negative PREs were measured at least once, including one event in which the outlet concentration was 28 times the inlet concentration (Table A4). Median PREs of dissolved copper for these studies ranged between -32% and +84%, with an overall median PRE of +24% for all sites (Table 5). The PRE of dissolved copper was negative at least once in 10 of the 12 studies, and the median PRE for all paired data sets for four individual studies was negative (Table A5). The width of grassy strips influence how well they treat runoff; however, the relation between PRE and width is not linear. In several studies, PRE were maximized within 5 meters of the edge of pavement; no improvement in PRE was demonstrated with wider strips (Barrett et al., 2004; CALTRANS, 2003).

Less data are available for grassy swales (Tables A4 and A5). PRE could be calculated from the BMP database for total copper in six studies and for dissolved copper in five studies. Median PRE for total copper ranged from +0% to +62%, and for dissolved copper ranged from -3% to 58% (Table 5). Negative PREs were observed at least once in four of the six studies for total copper and in four of the five studies for dissolved copper (Tables A4 and A5). Overall median PREs across all grass swales were +38% and +5% for total copper and dissolved copper, respectively (Table 5).

Summary of Speciation, Transport and Attenuation of Copper from Roads

The runoff entering roadways contains copper from building materials, and possibly from residential use of lawn and garden pesticides. To this runoff, copper from brake pad dust and tire dust is added. A significant fraction of the brake pad dust is less than 0.1 um (nanoparticles). A bridge study in Seattle indicates that very little of the copper estimated to have been released by vehicles (0.2 to 4%) is washed off controlled roadway access during rain events (Table A3) or is accumulated on the residential streets in West Seattle during dry periods. In contrast, the amount of copper that accumulated in Southwest Seattle streets represented between 52 and 162% of copper released from vehicles during two months, possibly indicated a source of copper to the streets other than vehicle wear material. Little of the copper released by vehicles is removed as coarse material collected during street sweeping and catch basin clean operations.

During wetter weather, about 50% of the copper in roadway runoff from residential areas is in the dissolved phase (Table A3). Total concentrations and the percentage of copper in the particulate phase increase with increasing TSS. Median PRE of 53% and 38% of the total copper have been measured as roadway runoff flows over grass strips and through grassy swales to stormwater systems, respectively (Table A4). Less dissolved copper was removed by grass strips and grassy swales, 24% and 5%, respectively (Table A5).

Like temporarily settled solids in stormwater pipes, copper previously removed from the flow stream in a variety of stormwater infrastructures can easily be mobilized under certain storm conditions. The attenuation of copper in stormwater systems within a basin is highly dependent on the types of stormwater systems present. Curbed roadway, where road runoff flows directly through pipes, will experience little attenuation. In contrast, the degree of attenuation of copper flowing off uncurbed roadway will depend on both the landscape (gravel, grass strips or grassy swales) and the configuration of BMPs (width of grass strips).

From Stormwater to Urban Streams

Stormwater containing roof and road runoff flows down drains to catch basins, through pipes, through BMPs, such as retention ponds, detention ponds and vegetated channels, and into urban streams (Figure 3). Contaminants in the solids removed from catch basins are usually disposed in landfills. The conveyance system for stormwater is usually impervious, and settling of particles may temporarily reduce contaminant loadings, but these settled solids can be mobilized during heavy rainfall. Settling of particles and infiltration of water through the pervious surfaces of certain BMPs can attenuate contaminants.

Partitioning

Sansalone et al. (2010) found that the distribution of metals on particles varied between five eastern U.S. cities (Table A3). The percentage of copper in the dissolved phase in urban stormwater (Table A3) ranged from 21% to 68% in an eastern U.S. city (Owens-Mills, MD) where the TSS ranged between 29 and 278 mg/L (Camponelli et al., 2010). Artina et al. (2006) observed a strong correlation between concentrations of total copper and other COCs and concentrations of TSS.

Transport and Attenuation

Within the grassy ditches and swales, catch basins, detention ponds, vegetative channels and other infrastructures of stormwater conveyances, COCs can be retained, which will temporarily decrease their loadings to urban streams. Percent removal efficiencies for grass swales and grass strips were presented in the section on road runoff.

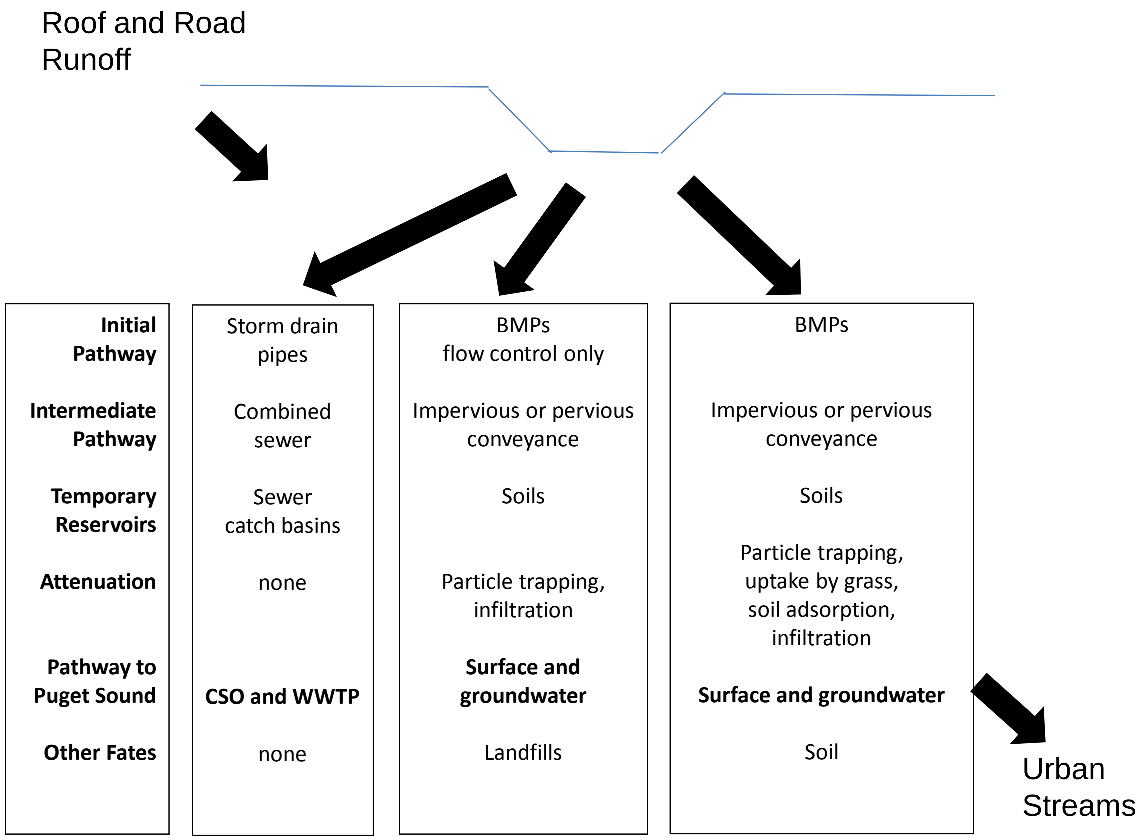

Figure 3. Pathways and fate of contaminants in urban stormwater.

Detention and retention ponds

Dry detention ponds are engineered ponds constructed mainly to detain water temporarily during storm events to reduce flow. The construction of the detention ponds is varied and includes concrete vaults, concrete basins with open surfaces and grass-lined detention ponds. The reduction of flow in the detention ponds can result in settling of particles and reduction in loadings of COC in urban streams.

Removal efficiencies were calculated for 61 events (Tables A6 and A7) as part of six studies of dry detention ponds (International Storm Water BMP Database, 2010). The median PRE for total copper for six studies ranged from -4% to +61% (Table 5). Negative removals of total copper were measured at least once in four of the six studies (Table A6). Removal efficiencies of dissolved copper were measured in five of these six studies (Table A7). Median PRE of dissolved copper for specific studies ranged from -9% to 17% (Table 5). All five studies had zero or negative PRE at least once (Table A7).

In addition to detaining water, wet retention ponds are constructed to reduce loadings to urban streams either through capture by plants or infiltration of water into groundwater. Removal efficiencies were calculated for eight surface ponds with a permanent pool, including one from

Bellevue, WA (Table A6). The overall median PRE for total copper from these studies was 42% and ranged from 0 to 72% for the eight ponds (Table 5). Retention ponds were less effective in capturing dissolved copper (median PRE of 18% with range from 16% to 20%).

A specialized case of a detention pond is a wet vault (Table 5). Wet vaults are usually constructed of concrete and engineered to reduce peak flows during storms. In Lakewood, CO, the median PRE in three wet vaults was 22% for total copper and 18% for dissolved copper.

For detention ponds, retention ponds and wet vaults, PRE of total copper was usually higher than dissolved copper. This observation indicates that these BMPs are more effective in removing contaminants associated with particles. Several investigators have examined sediments in various depositional areas within the storm systems to infer attenuation with the stormwater system. Camponelli et al. (2010) found elevated copper and zinc concentrations in retention ponds relative to background soils and found that most of the copper and zinc in the retention pond sediment was not released during moderately harsh chemical extraction procedures. This result would suggest that the most of the copper and zinc was likely not bioavailable. The distribution of particulate matter and particulate metals was dependent both on site and on the event within the site (Sanslaone et al., 2010).

Summary of Speciation, Transport and Attenuation of Copper in Stormwater Systems

The partitioning of copper in stormwater systems, and thus its attenuation of copper, is highly dependent on TSS concentrations. The percent removal efficiency of total copper in stormwater BMPs was highly variable and dependent on the type of BMP. Like the roadway BMPs, percent removal efficiencies of dissolved copper were less than that for total copper. Additions of total copper from BMPs were not infrequent; suggesting that copper removed in BMPs during specific events can be remobilized under certain storm conditions.

In Urban Streams during Storm Events

Once stormwater enters urban streams, settling of particles is the primary mode of attenuation for most contaminants. Infiltration can occur in losing reaches and the hyporheic zone (Figure 4). The majority of research on copper and other COCs in urban streams during storm events focused on the status of COCs in the stream (concentration, partitioning and concentration on particles) rather than the fate of COCs in urban streams. In the next few years during which the results of the first round of effectiveness monitoring conducted under the Phase 1 Municipal Stormwater Permits in the state of Washington are synthesized, knowledge of the attenuation of COCs in specific engineered structures is likely to greatly increase.

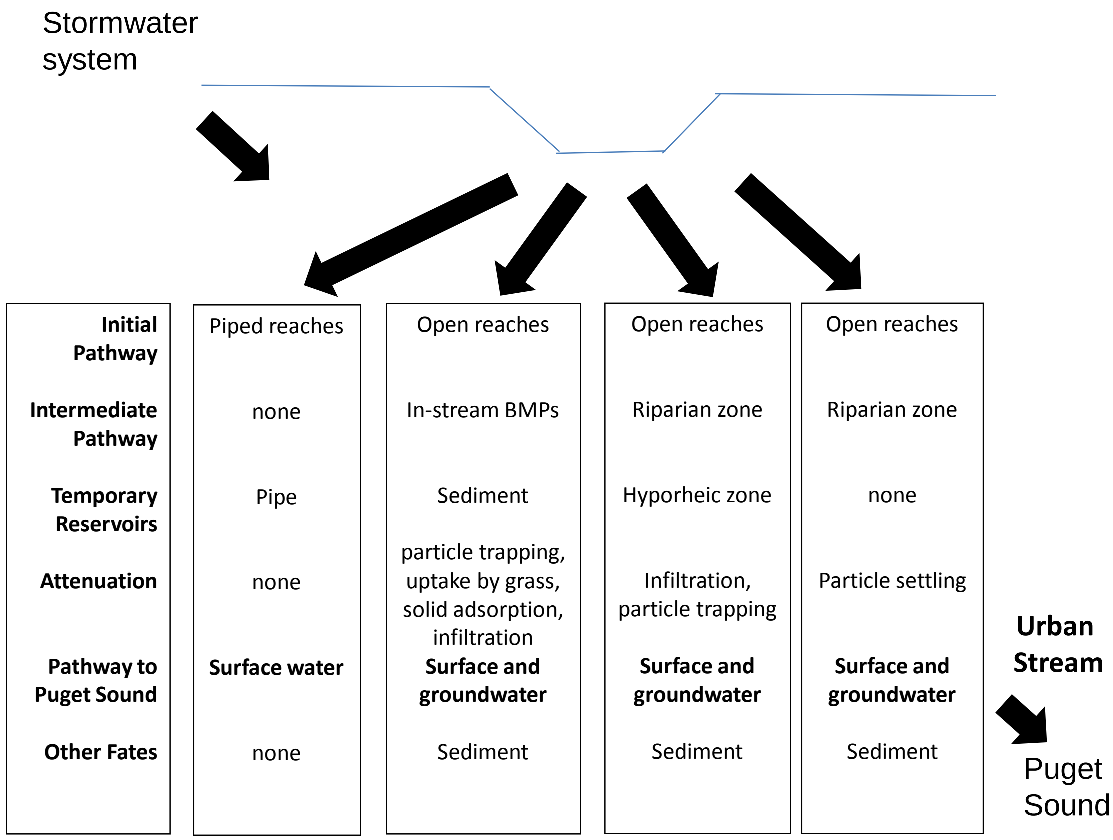

Figure 4. Pathways and fate of contaminants in urban streams.

Partitioning

Data on both dissolved and total metal concentration in Ecology's Environmental Information Management System (EIM) database (Ecology, 2010) for numerous sites throughout Puget Sound area could be used to calculate partitioning of metals in urban streams. However, the analysis of these data requires an understanding of the environmental conditions for each sampling event in order to arrive at any meaningful conclusions. The May 2011 publication of the surface water runoff study (Herrera Environmental Consultants, Inc., 2011) and data collected in receiving waters of stormwater systems being released as part of municipal stormwater management programs is likely to provide more environmental data to evaluate partitioning of copper in urban waters. The partitioning of copper during three storm events in Mill Creek and 32 events in Thornton Creek are presented as part of the Copper Case Study.

Attenuation and Transport

In water courses that are piped, it is unlikely that COCs would be permanently retained. However, COCs in the particulate phase may temporarily settle, but may be scoured during higher flow periods. In some urban streams, the path of the urban stream is actually a BMP structure such as grassy swales, wetland channels, and detention ponds previously discussed.

The nature of the stream riparian zone will also affect attenuation by particle trapping and flow modification. Vegetated stream banks will not only trap contaminants on particles as water levels rise during higher flows, but will slow flows by friction of the vegetation and enhance in-stream settling of particles. In contrast, concrete channels and rip-rap banks provide little opportunity for particle trapping and less friction to slow stream flow.

Another potential attenuation pathway within streams is in-stream processing in the water column or in the hyporheic zone, the saturated area of the streambed area where groundwater and surface water mix. The importance of the hyporheic zone of streams has become more evident in recent years. Research has shown that the presence of large woody debris, in-stream vegetation, channel meanders, and pool-riffle sequences all have potential to increase hyporheic exchange in streams (Valett and others, 2002; Harvey and others, 2003; Boano and others, 2006; Gooseff and others, 2006). Therefore, streams with higher degrees of habitat heterogeneity (complexity) have a higher potential to temporarily retain (and possibly treat) water. Conversely, streams with low habitat complexity, such as concrete channels, transmit water more directly with less potential for treatment of the water, as is the case for nutrients (see Grimm and others, 2005).

Summary of Speciation, Transport and Attenuation of Copper in Stormwater Systems

Similar to in-line stormwater BMPs, attenuation of copper through in-stream BMPs are affected in two ways: 1) attenuation is dependent on the partitioning of copper, with attenuation of particles being greater than attenuation of aqueous phase copper, and 2) removal of copper from the stream may be temporary; the copper could become remobilized under certain storm conditions. The nature of the riparian and hyporheic zones also affects particulate trapping and flow alteration.

Puget Sound Case Study of Copper

The goal of this case study is to use a mass balance approach to determine the fate of all the estimated unconstrained copper releases into specific basins (Ecology, 2011b). The fates of the released copper include transport out of the basin by winds, settling within the soils and sediment in the basin, infiltration into groundwater, capture by street sweeping and catch basin cleanout programs or by combined stormwater-sewer system, or transport by surface water in stormwater structures and creeks.

The ideal case study would examine longitudinal changes in dissolved and particulate copper concentrations in the creek in the context of additional sources, and transport and attenuation processes thought to be taking place in the larger basin. For instance, Paulson et al. (1984) measured dissolved and particulate copper concentration along 11 km of the Green-Duwamish River and observed flocculation of dissolved copper in the salt wedge of the Duwamish Estuary.

The majority of the surface water data available in the Ecology's Environmental Information Management database (Ecology, 2010) database is monitoring data at a single sampling location at the outlet of large basins and does not provide information on attenuation within the basin. In addition, the lack of daily traffic data and data of roof-top areas that are needed to calculate releases of total copper further limits the basins for this case study to the few basins with data that allow calculation of basin loadings. Thus, case studies are limited to comparing the releases of total copper in large basins (tens of km^2) to the loadings of total copper at the mouths of the creeks (Figure 5). Discrepancies between estimated releases and creek loadings must be inferred from literature studies and the available basin-specific data on the fate of copper within the basins.

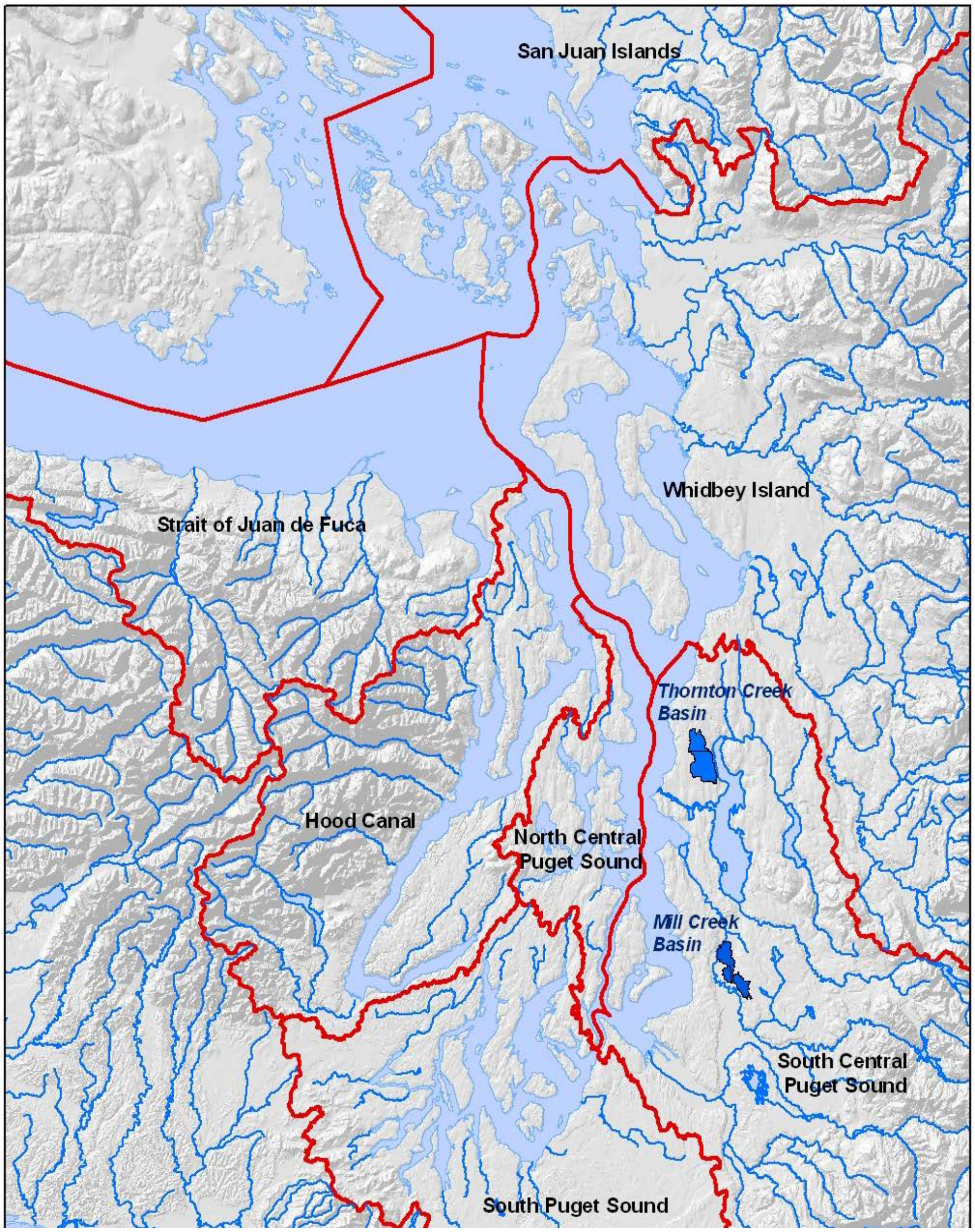

Figure 5. Location of Mill Creek and Thornton Creek basins**.**

The red lines identify the Puget Sound action areas.

The Mill and Thornton Creek basins (Figure 5) for the copper case study were selected based on the availability of land use and other basin-specific data, as well as chemical data concentrations of total copper and other ancillary constituents. Ecology (Golding, 2006) collected hourly samples near the mouth of Mill Creek in Kent during three 2-day storms with long antecedent dry periods (11–17 days) in 2005. King County Department of Natural Resources (Deb Lester, 2010) collected a single grab sample at the mouth of Thornton Creek in Seattle during 32 storms of varying duration and antecedent dry periods between 1998 and 2010.

The drainage area of Thornton Creek basin in Seattle and Shoreline is about 50% larger than the drainage area of the Mill Creek basin (Table 6). The average long-term flow of Mill Creek is about 50% higher than Thornton Creek. With its small size relative to Thornton Creek, the unit area runoff of Mill Creek is twice that of Thornton Creek. The Mill Creek basin is more commercial, including large areas of commercial car lots, and industrial than the predominately residential Thornton Creek. Hydrological features important to understanding attenuation in the Mill Creek and Thornton Creek basins are described in Appendix A.

Table 6. Characteristics of Thornton and Mill Creeks.

	Mill Creek	Thornton Creek
Land Use		
Total drainage area (km^2)	20.5	30.0
Forest/Field/Other (percentage of total)	22	14
Commercial/Industrial (percentage of total)	53	12
Residential (percentage of total)	25	74
Area in which Particles are More Likely to Settle		
Low-gradient near outlet (percentage of total)	65	2
Variables Driving Copper Release		
Total roof area (km^2)	3.56	4.79
Average Daily Vehicle Miles Traveled	577,500	1,371,800
Controlled access	153,400	893,400
Arterial and neighborhoods	424,100	478,400
Hydrologic Characteristics		
Flow, 9 year average 2000-2008 (m^3/s)	0.39	0.25
Unit area runoff (m/yr)	0.60	0.27

The methods for estimating the release of copper from road and roof sources is described in detail in Appendices B and C, respectively. For the road sources, the average daily vehicle miles traveled (ADVMT) was calculated from available traffic flow data for each basin. For each storm event for which copper data was collected (Table A8), the dry antecedent period was determined by local precipitation data. The total number of vehicle miles traveled (VMT) corresponding to each storm event was obtained by multiplying the ADVMT by the sum of the days of the storm event and the antecedent dry period. The amount of copper released for each storm event was estimated by multiplying VMT by a value of copper release/VMT (1.01 mg/VMT for Ecology, 2011b).

It should be recognized that the magnitude of the unaccounted copper is uncertain because copper release from brake pad wear "is highly uncertain due primarily to the difficulty obtaining reliable estimates of wear rates" (Ecology, 2011b). An alternative unit vehicle release (0.03 mg/VMT) for controlled access roads (from the 520 Study in Table 4) and for arterials (0.59 gm/VMT) from San Francisco (Rosselot, 2006) is used to assess the sensitivity of the estimated releases to the unit vehicle release value considered.

In the release model used here, copper is thought to be washed off the streets during storm events of a specific threshold (0.13 cm rainfall in this report). For a given basin where ADVMT is fixed, the model for release of total copper from vehicles for a particular storm event is a function of the time period between the end of the last storm and the end of the storm being monitored. This time period is the sum of the duration of the storm and antecedent dry period.

For the roof source, a copper concentration for each specific land use [$(TCu)_{LC}$] was taken from Ecology (2011b) and is shown in Table 7. These copper concentrations for each land use were then multiplied by the total volume of rain falling on roofs in each land use category per storm event, derived from local weather stations, and summed to estimate the copper loading for the basin. For a given land use, release of total copper from roofs for a given storm is a function of total rainfall during the storm event.

Table 7. Concentration of total copper for each land cover and roof areas in Mill and Thornton Creek basins by land use.

	$(TCu)_{LC}$ (ug/L)	$(Area)_{SA,LC}$ (km^2)	
		Study Area (SA)	
Land cover (LC)		Mill Creek	Thornton Creek
Forest/Field/Other	**31**	0.02	0.02
Commercial/Industrial	**90.7**	2.28	0.9
Residential	**23.3**	0.77	3.77
Total	--	3.07	4.69

$(Area)_{SA,LC,}$ = Roof area for specific study area (SA) and Land Cover (LC)
(TCu) = Total copper

Mill Creek

Estimated Releases

About 420,000 vehicle miles were traveled daily on arterials and neighborhood streets in the Mill Creek basin (Figure 6) and about 153,000 miles were traveled daily on controlled access SR-167 (Table 6 and Table A9). Combined with an antecedent dry period of between 11 and 17 days (Table A8) and unit vehicle release used by Ecology (2011b), between 6,972 and 10,457 grams per storm event were estimated to have been released by vehicles within the Mill Creek basin (Table 8 and Table A10). Using the alterative unit vehicle release [0.03 mg/VMT for controlled access roads from the SR-520 Study (Table 4) and 0.59 gm/VMT for arterials from San Francisco in Rosselot (2006)], the event total copper release was estimated to have been between 3,058 and 4,587 grams. The estimated release from roofs is defined by the total rainfall and ranged between 1,648 and 2,445 grams for the three storms.

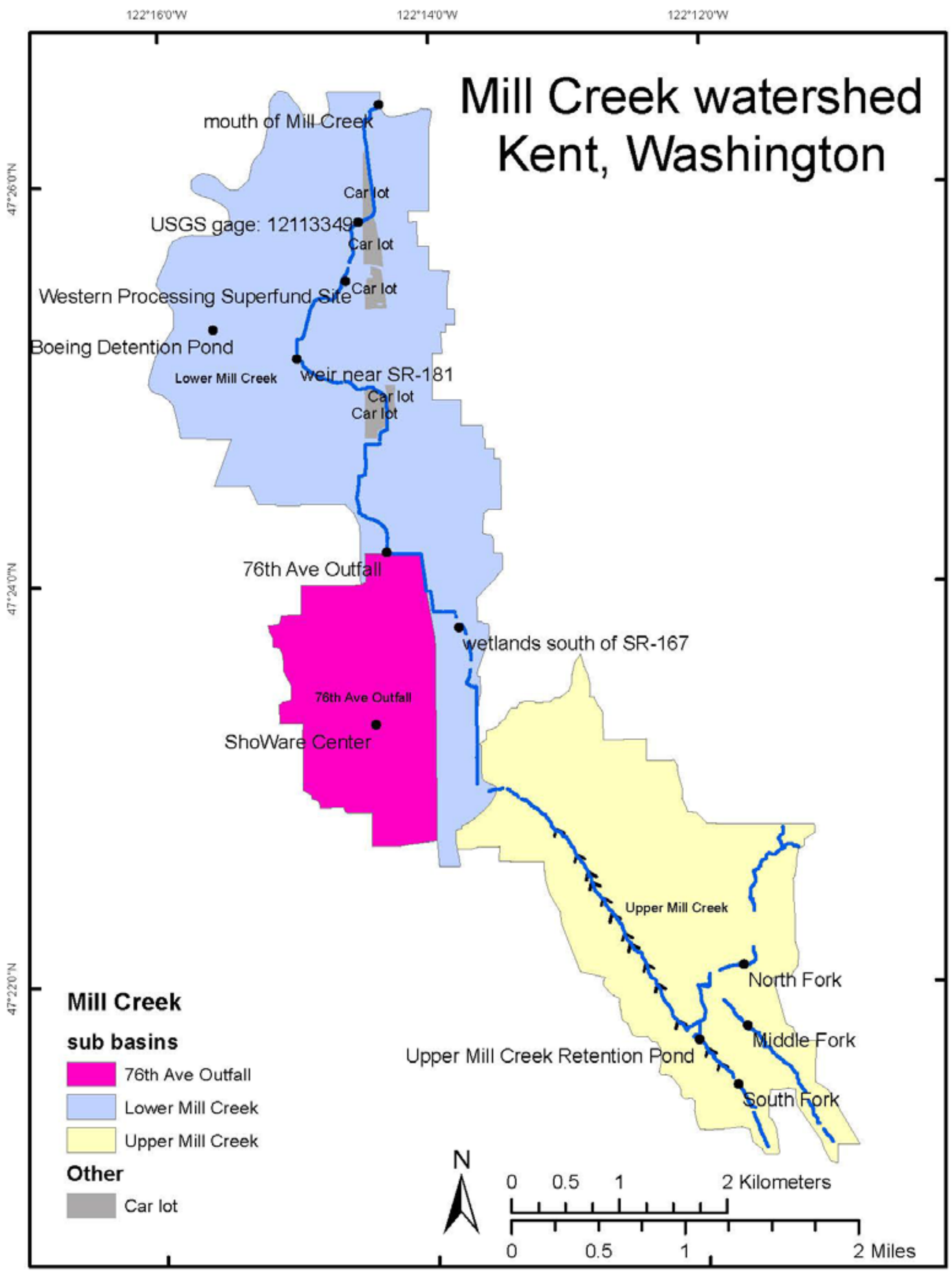

Figure 6. Map of Mill Creek basin in Kent, Washington.
Arrows on creek (<) show stream segments with downward gradient towards the floodplain. See Appendix A for narrative.

Table 8. Summary of ratio of total copper releases from roofs and roads to total copper loadings in Mill and Thornton Creeks during 36 storm events, 1998-2009.

Road Loadings (grams of total copper)[1]			Roof Sources		Storm Events		Basin Water Retention	Percentage of estimated releases of total copper not discharged by creeks during the storm event	
	Ecology Release	Alternative Release	Rainfall (cm)	Event Loading (g)	Total Copper Concen-tration (ug/L)	Stream Event Loading (g/event)		Ecology	Alterna-tive
MILL CREEK									
	Short storms (2 days) 11-17 day antecedent period, 3 sample days, 2005								
Range	6972 - 10457	3058 - 4587	0.73 - 1.08	1648 - 2445	0.94 - 13.6	110 - 153	82 - 86	99 - 99	97 - 98
Median	9295	4077	1.07	2415	4.8	127	86	99	98
THORNTON CREEK									
	Short Storms (1-2 days), 1-7 day antecedent period, 16 sample days, 1998-2008								
Range	1380 - 10581	309 - 2370	1.15 - 4.07	1961 - 6914	4.2 - 15	348 - 729	84 - 92	93 - 96	83 - 91
	Short storms (1-2 days), 7-36 day antecedent period, 4 sample days, 1998-2007								
Range	10351 - 51063	2318 - 11436	0.23 - 2.72	385 - 4625	4.7 - 13	96 - 540	80 - 91	97 -1 00	94 - 99
	Moderate storms (2-3 days), 1-4 day antecedent period, 5 sample days, 1999-2005								
Range	4140 - 8280	927 - 1854	2.43 - 5.07	4137 - 8615	4.5 - 8.4	293 - 1161	86 - 94	89 - 97	83 - 95
	Moderate storms (2-3 days), 8-14 day antecedent period, 2 sample days, 1998, 2009								
Range	13341 - 20701	2988 -4636	3.4 - 3.7	5704 - 6348	4.6 – 7.0	388 - 1376	82 - 92	93 - 99	85 - 96
	Large Multi-day Storms, 4-14 day antecedent period, 4 sample days, 2001-2009								
Range	12421 - 20701	2782 - 4636	2.48-14.64	4217 - 24883	2.8 2-8.0	359 - 3090	82 - 89	92 - 98	89 - 95
Median of 32 storms	5520	1236	2.46	4177	7.00	563	87	93	89

1) Ecology release is 1.02 mg/VMT; alternative release is 0.59 mg/VMT for arterials (Rosselot, 2006) and 0.03 mg/VMT on controlled access roads (Table 4).

Loads calculated in Mill Creek during three 2005 storm events

Extensive sampling of three 2-day storms in 2005 (August, September, December) provided total and dissolved copper and zinc concentrations every 1-3 hours, with increased frequency during peak flow (Golding, 2006). The sample location was located near the U.S. Geological Survey (2010) stream gage 12113349 in Figure 6) for which continuous flow data were available. The median total copper concentration during the three storms in Mill Creek was 4.8 ug/L (Figure 7 and Table 8) and a mean total copper concentration of 5.7 ug/L (Table 9). The median dissolved copper concentration was 3.1 ug/L (Figure 8), whereas the mean dissolved copper concentration was 4.1 ug/L (Table 9). The median fraction of copper in the dissolved phase was 70%, while the slope of dissolved copper concentration versus total copper concentration was 0.785 and was statistically significant (Table 9).

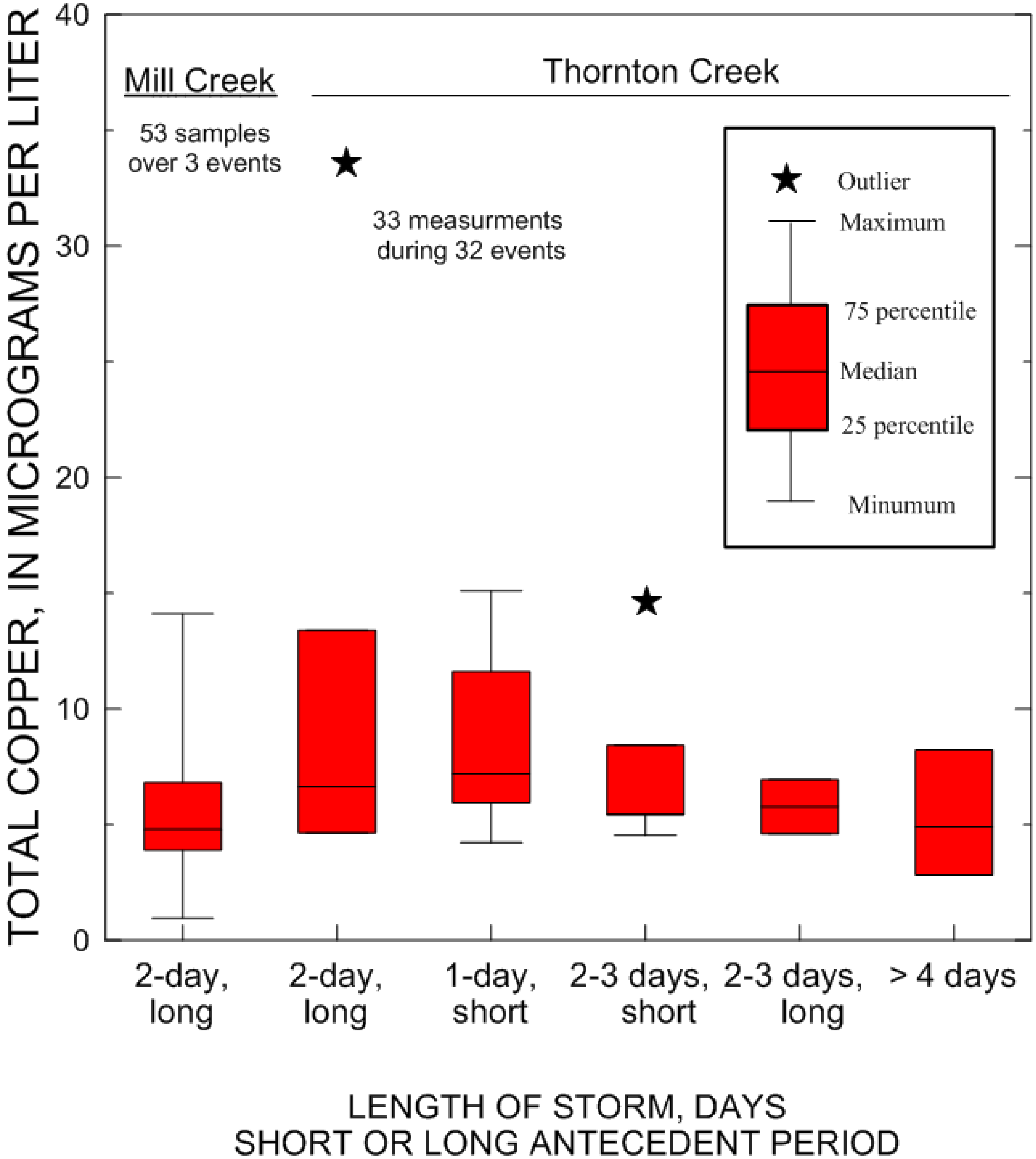

Figure 7. Box plots of total copper concentrations in Mill and Thornton Creeks during the storm events examined.

The asterisks indicate the two outliers described in the text.

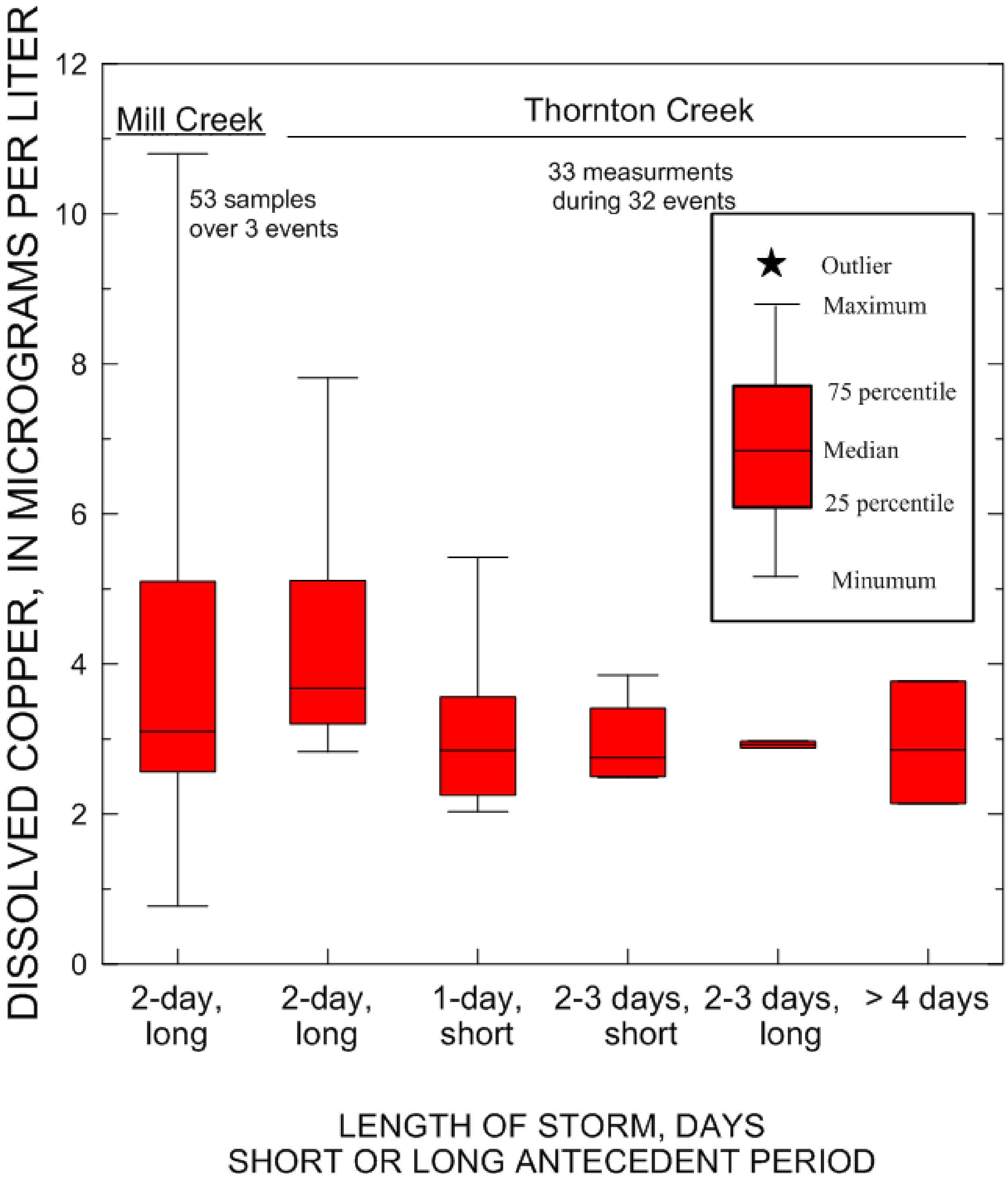

Figure 8. Box plots of dissolved copper concentrations in Mill and Thornton Creeks during the storm events examined.
The asterisks indicate the two outliers described in the text.

Table 9. General chemistry, mean concentrations and correlations of copper in Mill and Thornton Creeks.

	Mill	Thornton
General Chemistry-averages		
Total suspended solids (mg/L)	NA	56.0
Turbidity (NTU)	15.6	20.7
Hardness as CaCO3 (mg/L)	68.2	52.4
General Chemistry Correlations		
Slope: Hardness vs. flow	-2.76	-0.841
R^2: Hardness vs. flow	0.367	0.306
Mean Copper Concentrations		
Total Copper (ug/L)	5.7	9.3
Dissolved Copper (ug/L)	4.1	3.3
Total Copper Loading (kg/yr)	49.8	208
Mass ratio: dissolved copper to total copper	0.70	0.45
Copper Concentration on the Particles (mg/kg)	NA	119
Copper Correlations		
Slopes: Dissolved Cu vs. total copper	**0.785**	0.044
R^2: Dissolved copper vs. total copper	0.967	0.074
Slope: Total copper vs. flow	0.291	0.045
R^2: Total copper vs. flow	0.11	0.0057
Slope: Dissolved Cu vs. total suspended solids	NA	0.0013
R^2: Dissolved Cu vs. total suspended solids	NA	0.0053
Slope: Particulate copper vs. total suspended solids	NA	**0.105**
R^2: Particulate copper vs. total suspended solids	NA	0.976

NA=Not analyzed

The hourly loadings of total copper were calculated by multiplying the total copper concentrations by total hourly flow. The flow data reported in Golding (2006) was USGS provisional data, which since has been revised. The total copper event load in grams was given by the sum of the loads for each of the samples, applying the copper concentration to the preceding period. For the August 2005 storm, the total copper was not measured over the entire storm hydrograph; therefore, the event loading for the measured portion of the hydrograph was adjusted upward to account for the portion of the hydrograph for which total copper not measured. The loadings of total copper during the three 2005 storms ranged between 110 and 153 grams (Table 8, Figure 9).

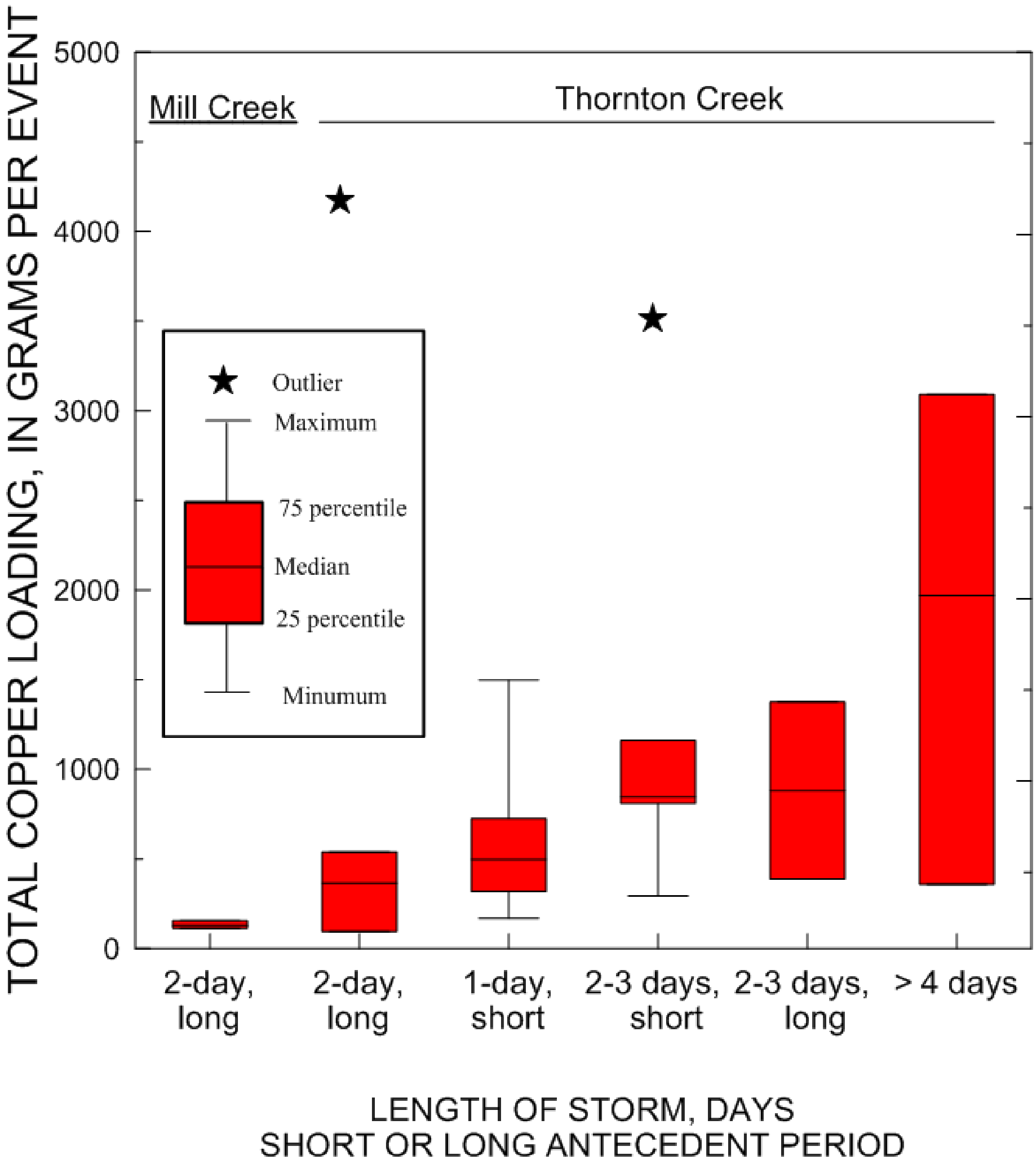

Figure 9. Box plots of loadings of total copper without two outliers.

Relation of estimated storm event releases to storm event loadings in Mill Creek

Since it is the water that falls on the basin that transports copper through the Mill Creek basin, it is informative to examine the fate of water that fell on the Mill Creek basin during the three storms. The total volume of water that falls on a basin is equal to:

Total rainfall volume (m^3) = basin surface areas (m^2) * rainfall (cm) * (1 m/100 cm) (eq .4)

Using the basin area of 20.52 km^2 (Table 6) and the event rainfall (Table A8), between about 150,000 and 220,000 m^3 fell on the basin during the three storms. The total discharge volume for each event was calculated by integrating the flow of Mill Creek over the duration of each storm event, which resulted in discharges between about 20,000 and 40,000 m^3. Comparing the total discharge volume to the total rainfall volume indicates that only 14% to 18% of the water falling on the basin flowed from Mill Creek during the storm and that the basin retained between 82% and 86% of the water (Table 8).

The estimated copper releases within the Mill Creek basin under the two release scenarios were compared to the loadings of total copper at the mouth of Mill Creek during the three monitored storm events. The difference between the estimated releases and calculated loadings cannot be characterized as attenuation because attenuation is defined as reductions in loading in fluid flow.

The estimated released copper that was not transported to the mouth of Mill Creek cannot be said to be attenuated, especially since no samples were taken upstream in the basin to affirm that the estimated released copper actually entered the surface water system. In addition, an unknown portion of the released vehicle wear materials is transported out of the basin as wastewater from commercial car washing facilities, as street dirt from street sweeping and catch basin cleanout programs or as atmospheric dust. Using the same form of equation as equation 3, we define the term "Percentage of the estimated released copper not transported by Mill Creek" as:

$$\text{Percentage of the estimated released copper not transported by Mill Creek} = 100 * \left(1 - \frac{\text{copper loading}}{\text{estimated release}}\right) \quad \text{(eq. 5)}$$

Between 97% and 99% of the estimated released copper was not transported by Mill Creek during the durations of the three storms. This large difference between estimated release of total copper and loadings of total copper in Mill Creek could be caused by 1) an overestimation of release of total copper, 2) transport of total copper out of the basin as wastewater, street dirt and atmospheric dust, 3) permanent or temporary retention of particulate copper in soil and sediment reservoirs of the basin, and 4) delayed transport of dissolved copper to the creek as groundwater.

Possible fate of copper released into in the Mill Creek basin

Of the possible fates of copper estimated to have been released within Mill Creek basin that was not transported by Mill Creek during the storm events, only the amount of copper in solids sent to the landfill collected during street sweeping and catch basin cleanout programs could be estimated. The fate of the remaining copper that is not captured by street sweeping and catch basin cleanout programs or transported to the mouth of Mill Creek can only be inferred by applying data in the literature to specific features within the Mill Creek basin.

In the remainder of this section, the authors use observations in the literature and their best professional judgment to infer the fate of unaccounted copper in Mill Creek in the four segments of the pathway of roof and road runoff to Mill Creek. It should be recognized that the magnitude of the unaccounted copper is uncertain because copper release from brake pad wear "is highly uncertain due primarily to the difficulty obtaining reliable estimates of wear rates" (Ecology, 2011b).

Fate of copper in roof runoff

Copper in roof runoff from the downspout can be affected by a number of attenuation processes depending on the route to the stormwater system or the roads. Roof runoff piped **directly** to the storm water system and gutter, as occurs throughout much of downtown Kent, enters the road drainage system with no attenuation.

Copper in roof runoff flowing from the downspout to either impervious surfaces adjacent to the building or onto pervious surfaces (e.g., lawns or grassy swales) in some of the older sections of Kent can be attenuated by a number of physical and chemical processes. There is likely no long-term accumulation of particulate copper on driveway and other impervious surfaces since the detained particles are likely mobilized by the turbulence of the overland flow during higher intensity rain and entrained in the runoff entering the stormwater system.

For the roof runoff that flows over lawns or into grassy swales, the runoff and its dissolved constituents can infiltrate into the groundwater system or the particles can be trapped by soils during infiltration or by vegetation during overland flow. Roof runoff from many newer commercial areas in Kent is diverted to retention ponds and only emerges as groundwater during baseflow conditions. Some of the copper infiltrating into the aquifer will be absorbed by mineral or organic surfaces and the remaining copper will emerge to surface waters in groundwater that contribute to base flow. In much of the newer developments in Upper Mill Creek, roof runoff is routed to on-site infiltration systems, in which copper is highly attenuated.

In contrast to light rainfall, heavy, turbulent overland flow over landscaped areas can cause erosion, such as that measured at the campus in Storres, CT (Boulanger and Nikolaidis, 2003). If soils are enriched in copper because of application of sewage sludge, inorganic fertilizers, or pesticides or due to accumulation from atmospheric deposition (local or regional), erosion will magnify the loadings of copper to the stormwater system.

The majority of particles transported down the downspout probably get trapped in drain lines, on impervious surfaces, and in the soils of lawns during light rain, leaving copper mainly entering the roads in the dissolved phase. With increasing rainfall, overland flow begins to mobilize these temporary reservoirs of copper in pipes and on impervious and pervious surfaces and starts to erode soils, some which may contain higher copper concentrations due to application of biosolids, fertilizers and pesticides. Once roof runoff enters the road drainage system, it combines with copper released from vehicles and is transported to Mill Creek by a variety of conveyance systems.

Fate of copper from vehicles
Copper, antimony and iron from vehicle wear material (brake pad dust and tires) are released as vehicles travel on urban arterials and controlled access highways. The literature provides a number of insights into the fate of copper released as brake pad dust. Much of the copper released from brake pads is thought to be emitted into the air as dust, some of which would to be incorporated into the regional air transport system or be deposited evenly across the landscape as precipitation or transported out of the Puget Sound airshed. Some of the atmospherically transported copper will settle on road shoulders or right-of-ways, to be mobilized during storm events or likely be incorporated into general soils. Significant amounts of the copper brake pad dust may remain on the wheel assembly, including accumulating on hub caps. The fate of this copper will depend largely on the car washing habits of the Puget Sound residents.

Several observations previously described suggest that not all of the copper released from vehicle wear material accumulates on Puget Sound roads and is **not directly** transported to urban streams during storm events. Data from the literature suggest very little of the brake pad dust initially settles on the street and most of it accumulates in right-of-ways, shoulders and adjacent lawns. This copper is a temporary reservoir that can be mobilized during storm events.

The amounts of copper collected by street sweeping and catch basin cleanout programs were estimated by applying copper concentrations and unit efficiencies derived from the City of Seattle Street Sweeping Report (Seattle Public Utilities and Herrera Environmental Consultants, 2009) to the miles of curbed road and the miles of swept roads within the Mill Creek basin. Approximately 30 grams of copper in the Mill Creek basin is removed each day by street sweeping, based on the number of miles of roads swept in the City of Kent and the efficiency of copper removal in Puget Sound (Seattle Public Utilities and Herrera Environmental Consultants, 2009) and 9 grams per day was removed from catch basins along curbed roads. Amounts of copper that remain on roads will be mobilized and transported to the stormwater system with increasing intensity of rainfall.

Fate of copper in the Mill Creek stormwater system
In the piped sections of the Mill Creek in Kent, the solids can temporarily settle in catch basins and in the storm drains and be remobilized during larger storms. In much of the residential area of the residential areas of Upper Mill Creek in Kent, stormwater is transported in roadside ditches and vegetated channels flowing through open space.

Literature BMP data indicated that a portion of total copper (Table A4) and to a lesser portion of dissolved copper (Table A5) is removed in grassy roadside ditches. The more recent construction in Upper Mill Creek allowed preservation of the riparian buffers around Mill Creek and its tributaries to the extent that some creek segments function as wetlands. The efficiency of removal of total copper in constructed retention facilities, such as the Upper Mill Creek Retention Pond and the Boeing Detention Pond, is about 42% while that of dissolved copper is less than 20% (Tables A6-7). Much of the copper released in Upper Mill Creek either from roofs or from vehicles probably resides along roads and in vegetated stream segments.

Once stormwater enters the main branch of Upper Mill Creek below the retention pond, Upper Mill Creek flows through a steep ravine where attenuation is minimal. Upon reaching the flood plain, the gradient of Upper Mill Creek levels and several natural segments, such as the wetlands south of SR-167 in Kent, provide areas of decreasing flow where particles containing copper will settle and some dissolved copper may be trapped by biological processes. However, the net export of total copper from detention and retention ponds reported in the literature (negative efficiencies in USGS Tables A3-A4) suggest that settled copper in these types of facilities may only be a temporary reservoir that can be mobilized into the stormwater system with increasing energy from intense and long duration storms.

Even under low flow conditions, highly turbid water is commonly observed being discharged from the S. 76th St. outfall to Lower Mill Creek, suggesting that attenuation of particles and copper in the stormwater system of downtown Kent is minimal. After the confluence with the 76th St. Outfall, Lower Mill Creek meanders through the gently sloping floodplain to its mouth.

Initially, Lower Mill Creek flows through open space, including along the Interurban Trail where overhanging blackberries and stream vegetation slow the flow of the creek and enhance particle settling. Lower Mill Creek then flows through more developed areas of car lots and office buildings where attenuation is less likely, except possibly from catch basin cleanout programs.

In a several block segment, Lower Mill Creek receives the roof runoff and parking lot runoff from the Kent Boeing Plant, which are filtered through constructed wetlands along SR-181 behind a weir that likely traps particulate copper and some dissolved copper. Just downgradient of the weir, Lower Mill Creek receives the discharge from the Boeing Detention Pond that captures some copper released from roads and roofs in this commercial area. From the weir, Lower Mill Creek flows through a commercial area and is buffered on both sides except for a small segment through a large car storage facility.

Like other flood plain segments of Lower Mill Creek, overhanging blackberries and macrophytes in the stream slow the flow and enhance particle trapping. This effective trapping of particles in the extensive network of roadside ditches, vegetated channels, retentions ponds and preserved riparian buffer adjacent to a long segment of Lower Mill Creek in the gently sloping floodplain is probably responsible for the dominance of dissolved copper in the copper loading observed by Golding (2006) during three modest 2-day storms following long antecedent dry periods in 2005.

Thornton Creek

Estimated Releases

The total event rainfall and antecedent dry period for 32 storms sampled by Lester (2010) were estimated from precipitation data from between two and four precipitation stations in north King County (Table A11). The variations in the estimated antecedent dry period for a single storm event in Thornton Creek using data among these north King County stations were greater than the variations for the Mill Creek basin derived from the three stations in south King County around Kent (Table 8). Two storms (September 18, 1998, and August 11, 2009) had antecedent dry periods greater than one month.

The ADVMT on arterials and neighborhood streets in Seattle (Table A12) and Shoreline (Table A13) and the controlled access I-5 (Table A14) were combined with estimated dry antecedent periods to calculate the total VMT in the basin before and during each storm event. The total VMT in the basin before and during the storm event were multiplied by the unit vehicle release (1.01 mg/VMT) to obtain estimated release of total copper from vehicles during the 32 storm events, which ranged between 1,380 and 51,300 grams. When the alternative lower unit vehicle release described for Mill Creek that takes into consideration differing braking patterns on controlled access I-5, the estimated release of total copper during the 32 storm events decreased by an order of magnitude and ranged between 309 grams and 11,500 grams.

Total rainfall among the three to four precipitation north King County stations in the vicinity of Thornton Creek basin were generally within 50% (Table A11). Rainfall for storms of short duration (1-2 days) ranged from 0.66 cm to 4.07 cm. In contrast, the total rainfall for the 7-day storm in November 2006 was 14.64 cm. The estimated release of copper from roofs ranged between 385 and 24,883 grams.

Copper loadings calculated in Thornton Creek during 32 storm events (1998-2009)

In contrast to the intense sampling of Mill Creek during three storms, single grab samples of water from Thornton Creek (Figure 10) were collected during 32 storm events between 1999 and 2009 (Lester, 2010). The total volume of each storm event was calculated by integrating the discharge under the storm hydrograph while assuring that the duration of the hydrograph used to calculate the copper loadings was consistent with the duration of the storm event used to calculate the copper releases. Total discharge volumes of Thornton Creek during the 32 storms ranged from 13,400 m^3 to 467,000 m^3.

The median total copper concentration was 7.00 ug/L and ranged between 2.82 and 36.5 ug/L (Table 8). Total copper concentrations tend to be lower with increasing storm duration. Two concentrations are considered outliers for their storm category (Table A10) and will be shown separately (36.5 ug/L collected on June 3, 2008, for the category of 1-2 day storm with long antecedent dry period and the 13.1 ug/L collected on May 5, 2009, for the category 2-3 day storm with short antecedent dry period). The June 3, 2008, sample was collected at the height of the first peak of hydrograph. The median of dissolved copper concentrations was 2.97 ug/L and ranged between 2.03 and 7.81 ug/L (Figure 8).

It is difficult to fully characterize the rapidly changing flow and chemical conditions in a stream by collection of a single grab sample during a storm event. Therefore, the total copper concentrations are not representative of the event mean concentration and the calculated loadings of total copper are likely to be highly variable. Even with this caveat, the loading of total copper does increase with increasing duration of storm category and the total rainfall (Figure 9). For short storms (1-2 days), similar to those measured in Mill Creek, the total copper loading from Thornton Creek ranged from 96 to 540 grams per storm event. The total copper loading from Thornton Creek during moderate storms ranged from 293 to 1,376 grams per storm event, while the total copper loading during multiday storms with variable total rainfall ranged between 359 and 3,090 grams per storm event.

The copper loading data from Thornton Creek were subjected to a multi-linear regression model with total event rainfall and the duration of the storm event as the independent variables, the controlling factors for the release algorithms for roof and vehicle releases, respectively.

The loading of total copper was a function of total event rainfall ($p \leq 0.001$) and was not a function of antecedent dry period ($p = 0.56$). The increasing total copper loading with increasing total rainfall is expected from data previously presented. In Table 8, the narrow range of retention of water within basin indicates that total discharge during storm events is related to total storm rainfall. Total copper loadings would be correlated with total discharge, and therefore total rainfall, if total copper concentrations were independent of flow. In Table 9, the correlation coefficient between total copper concentration and flow is shown as 0.006. The fact that total copper loading is not correlated with an antecedent dry period indicates that attenuation of copper from vehicle sources is significant or that the copper release model from vehicles needs refinement.

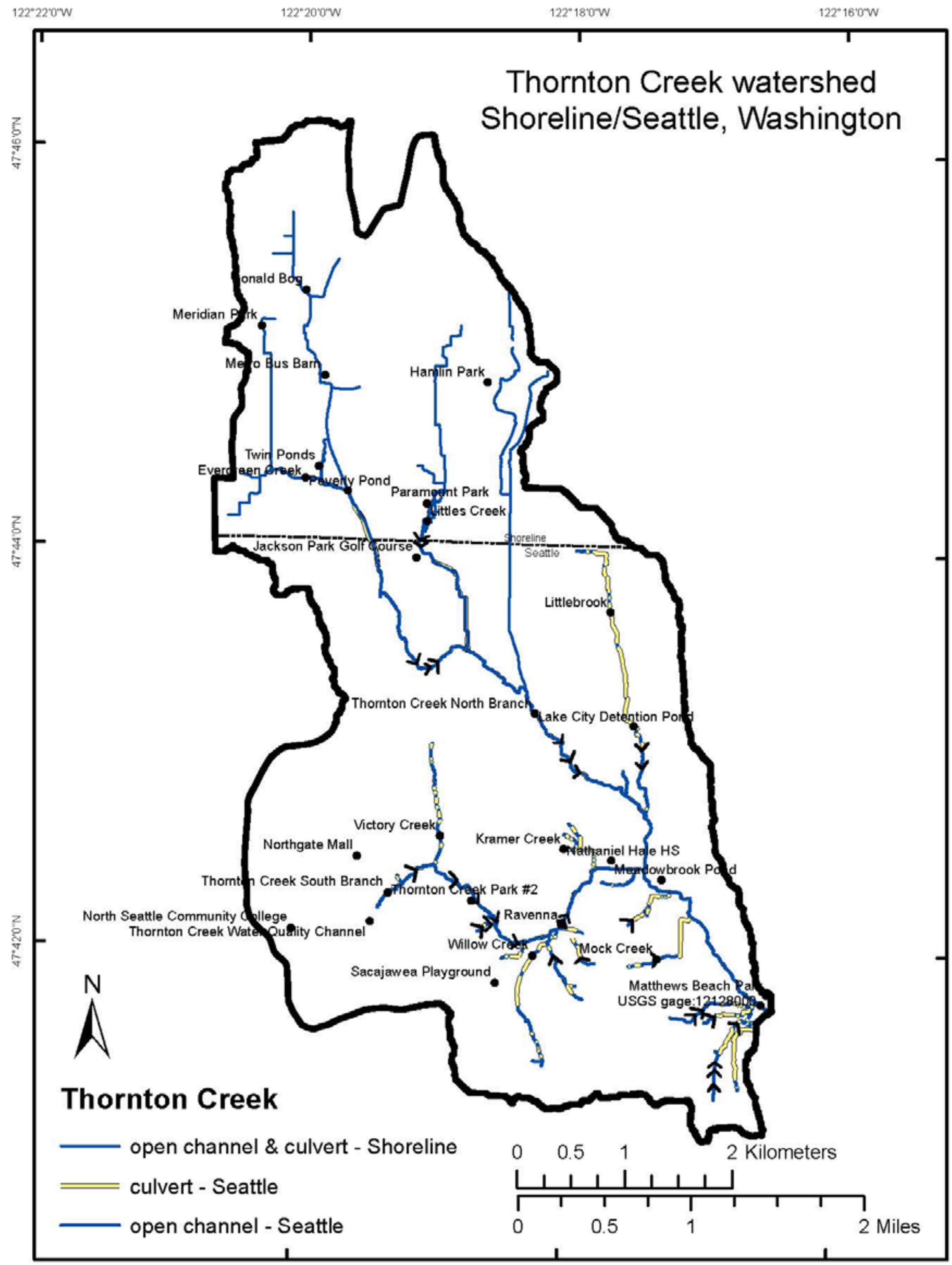

Figure 10. Map of Thornton Creek basin in Shoreline and Seattle, Washington.

Arrows on creek (<) show stream segments with downward gradient towards the floodplain. See Appendix A for narrative.

Relation of storm event estimated releases to storm event loadings in Thornton Creek basin

Similar to Mill Creek, the water budget of Thornton Creek indicates that about 87% (median value) of the rainfall was retained within the basin under a variety of storm conditions with water retention ranging between 75 to 94% (Table 8). Water retention does not seem to be a function of storm duration or total rainfall.

When the unit vehicle release value of 1.02 mg/VMT (Ecology, 2011b) is used to calculate estimated releases, a median value of 93% of the estimated amount of copper released into Thornton Creek was not transported to the mouth of Thornton Creek during the storm events (Table 8). The percentage of estimated copper not transported to the mouth ranged between 89% and 100%. When the lower unit vehicle release value that accounts for different driving habits on controlled access I-5 is used (Table 4), the median percentage of the estimated released not transported by Thornton Creek decreases to 89% with a range between 83% and 95%.

Fate of copper in Thornton Creek

The data on routes and frequency of street sweeping in the Thornton Creek basin in Seattle and Shoreline suggests that only a small amount of the copper released by vehicles is captured by street sweeping (13 g/day) and catch basin cleanout programs (6 g/day). In the absence of other rate data on copper accumulation for Thornton Creek or the Puget Sound, examination of studies in the literature and professional judgment can only provide insights into the fate of copper from brake pad dust released from vehicles.

Similar to the fate of copper in the Mill Creek basin, copper in roof runoff draining onto lawns in Thornton Creek (Figure 10) will be trapped in soils, while some of the copper flowing over impervious surfaces may be temporary retained during light rain. In the piped sections of the Evergreen, Littles and Hamlin Creeks, the North Branch of Thornton Creek in Shoreline, the Northgate area of the South Branch of Thornton Creek and the upper Little Brook in Seattle, the coarser solids are removed in catch basins and temporarily settle out in the storm drains. In much of the residential area of Thornton Creek in Seattle and small residential areas of Shoreline, stormwater is transported in roadside ditches that can sequester copper, especially particulate copper.

Constructed dry detention and wet retention facilities such Ronald Bog, Twin Ponds, Peverly Pond, and wetlands along Evergreen Creek in Shoreline, the irrigation and detention ponds in Jackson Park Golf Course, the Lake City Detention Pond, the "Thornton Creek Water Quality Channel" in Northgate area, and the Meadowbrook Pond in Seattle will capture both water and total copper and to less extent dissolved copper (Tables A3-A4).

In addition, several natural segments of Thornton Creek, Northwest Park #6 on the South Branch of Thornton Creek in Seattle and Paramount Park on the Littles Creek in Shoreline, may provide areas of decreasing flow where particles containing copper will also settle. However, the net export of total copper from detention and retention ponds (negative efficiencies in Tables A5 and A6) suggest that these facilities may only be a temporary reservoir of particulate copper that is mobilized back into the stormwater system with increasing kinetic energy from more intense and longer duration storms.

As stormwater flows down the steep gradient on the North and South Branches of Thornton Creek and leaves the Lake City Detention Pond on Little Brook Creek, no significant attenuation is likely to occur and stored copper in the streambed could be temporarily mobilized. In addition, these segments are prone to erosion that would release additional solids. Once flows in these highly armored channels reach the flood plain, the Meadowbrook Detention Pond is the only structure preventing the dissolved and particulate copper in the highly armored Main Branch from reaching the mouth of Thornton Creek. Since the Meadowbrook Pond is a detention pond designed primarily to control flows, retention of copper and particles may be minimal.

The mobilization of copper in the many temporary reservoirs and lack of opportunities for particle settling would explain why the loadings of copper in Thornton Creek during storm events are primarily in the particulate phase and solely a function of rainfall. The fact that the median concentrations of copper on the particles (115 mg/kg, respectively in Table 9) are well above the concentrations of natural soils (29-53 mg/kg in Table 3) indicates that the particles have been mobilized from anthropogenic reservoirs rather than the erosion of natural soils in the steep gradient segments approaching the floodplain.

Review of Transport Mechanisms and Attenuation of PCBs in Surface Water

The largest releases of PCBs are estimated to originate from large and small capacitors (Ecology, 2011b), which are likely contained in buildings, are leaked into drains connected to sanitary sewers, or are disposed of as solid waste due to general housekeeping or clean-up procedures. The release of PCBs in residential trash burning is an unconstrained combustion source to the atmosphere, and the fate of these PCBs includes transport out of the airshed, temporary storage in soils and sediments after landfall, or transport to surface waters from direct rainfall or from erosion of soil particles.

PCBs in electrical transformers that leak as liquids may fall onto pervious and impervious surfaces. PCBs in leakage from transformers falling onto pervious soils are likely adsorbed onto soils that act as a temporary reservoir for ground and surface waters. PCBs from transformers falling on impervious surfaces will eventually be transported to stormwater systems, overwhelmingly adsorbed to soil or sediment particles, that discharge to combined sanitary-stormwater systems or to surface waters.

In addition to transformers, industrial caulk used in the 1950s to 1970s contains PCBs that volatize and enter the regional atmospheric transport system through ventilation systems and open windows (Wallace et al., 1996; Menichini et al., 2007). Abraded caulk that falls indoors will likely enter the water or solid waste stream through general housekeeping procedures. Abraded caulk that falls onto pervious surfaces will likely be incorporated into soils that can leak PCBs into surface and groundwater.

Abraded caulk that falls on impervious surfaces will likely be transported as particulate matter, but once incorporated into stormwater and streams can dissolve into water. This can be confirmed by large bodies of water, such as the Great Lakes, where Franz et al (1998) report for Lake Michigan that the dry deposition of PCBs bound to particles is the dominate pathway, and the magnitude of dry particulate deposition is similar to that of the air-water exchange.

Foster et al. (2000) indicate that most of the transport of PCBs in urban stormwater is associated with particles. Once entrained in surface water, the fate of PCBs includes net volatilization (Rowe et al., 2007), temporary or permanent burial in freshwater sediment and transport to Puget Sound. Although degradation by photolysis in the atmosphere and microbial dechlorination in the sediment have been measured, degradation of PCBs in water has only been estimated from the physical properties of each PCB congener (Paasivirta and Sinkkonen, 2009).

The majority of data in the literature concerning PCBs in urban settings focuses on sediments, atmospheric deposition and body burden in aquatic organisms. The level of contamination of PCBs in urban stormwater mainly has been assessed by the collection of street dirt (Table 3). Irvine and Laganathan (1998) collected nine samples of street dirt in Buffalo, NY, and measured concentrations ranging between 90 and 1,700 ug/kg. In Bergen Norway, PCB concentrations in sediment collected in traps in stormwater systems ranged between 0.4 and 704 ug/kg (Jartun et al., 2008).

The measurement of PCB concentrations in urban waters is analytically challenging and expensive. Very little data are available on the concentrations of PCBs in urban streams. Since PCB concentrations in urban stormwater and streams are expected to continually decrease because of their restricted use, this study focuses on studies measuring PCBs in urban settings in the last decade (Table 10). In a study of Paris stormwater (Zgheib et al., 2011), PCBs were detectable only on filtered suspended particles and no PCBs were detected in filtered water above 30 ng/L.

During baseflow in the Anacostia River near Washington, DC (Hwang and Foster, 2008), total PCB concentrations ranged between 0.91 and 11.8 ng/L. During storm events, total PCB concentrations ranged between 9.8 and 211 ng/L. The partitioning between dissolved and particulate phases or total suspended solids concentrations were not reported, but total PCB concentration on the filtered particles ranged between 31 and 755 ng/g. In the larger Delaware River (Fikslin and Suk, 2003) and the Songhua River in China (You et al., 2010), total PCB concentrations ranged between sub-nanogram per liter concentrations to 14 ng/L.

Studies in the Houston Ship Canal (Lakshmanan et al. (2010) and the Delaware River (Fikslin and Suk, 2003) examined the longitudinal variations of PCB concentrations in urban waterways. These studies focused more on source identification of PCBs rather than attenuation processes affecting PCBs. Studies of the congener pattern in the heavily contaminated Hudson River system suggest that low molecular weight congeners may be lost by volatilization over the broad surface area of the New York/New Jersey Estuary (Panero et al., 2005). Volatilization in the Puget Sound watershed is most likely to occur in urban lakes with PCB water concentrations large enough that the gas exchange of PCBs is from the lake to the air.

Study findings emphasize that sub-nanogram per liter detection limits for filtered and unfiltered water and/or detection limits of less than 1 nanogram per gram (dry weight) on suspended solids are required to differentiate the effects of sources of PCBs from attenuation processes in longitudinal surveys of urban waterways. The need for even lower detection limits is emphasized for marine waters adjacent to major population centers because of their lower total PCB concentrations relative to urban stormwaters (Table 10).

Because of the challenges of directly measuring PCB concentration in water, much of the PCB water data are derived from passive samplers, such as semi-permeable membrane devices (SPMDs). SPMDs are closed segments of thin-walled, semi-permeable plastic tubing with a neutral lipid compound sealed inside.

A SPMD is deployed in the water column for a period of time, after which the neutral lipid compound is recovered and analyzed for a number of hydrophobic organic compounds, such as PCBs. The concentration of each PCB congener in the water is estimated from duration of deployment and from the rate of transfer across the semi-permeable member. The rate of transfer across the SPMD is calculated by calibration using site-specific conditions or using calculations provided by the manufacturer or reported in the literature. The calculated concentrations reflect exposure of PCBs in the dissolved phase to organisms, since it is unlikely that PCBs on suspended solids transfer across the membrane.

Table 10. Concentrations of PCBs in fresh, estuarine and marine surface water collected after 2000.

Location	Sample Dates	Fraction	Number of congeners included in sum	Total PCBs (ng/L)		Reference
				Mean	Range	
Freshwater						
Anacostia River, US	April - August 2002	Sum of separate filtered and particulate	85	--	0.91 - 11.8	Hwang and Foster (2008)
			85	--	9.8- 211	
Paris Suburb, France	February - March 2008	Sum of separate filtered and particulate	41	--	< 30 - 52	Zgheib et al. (2011)
		Filtered	41	--	--	
		Particulate	41	--	< 1 - 22	
Songhua River, China	April 2007 - January 2008	Unfiltered	Congener groups by selective ion monitoring	5.8	1.1 - 14	You et al. (2010)
Delaware River, US	September 2001 - March 2003	"Total PCBs"	--	--	0.43 - 10.1	Fikslin and Suk (2003)
Lake Michigan, US	--	Dissolved	--	0.15	--	Streets et al. (2006)
		Particulate	--	0.028	--	
Estuarine or Marine						
Off Barcelona, Spain	May 2001- June 2002	Filtered-subsurface	41	5.2	0.45 - 11.2	Garćia-Flor et al, 2009
		Particulate-subsurface	--	1.2	0.09 - 4.6	
Banyulus-sur-Mer, Spain	September 2001- July 2002	Filtered-subsurface	41	3.9	0.12 - 9.4	Garćia-Flor et al. (2009)
		Particulate-subsurface	--	1.8	0.14 - 7.8	
Hong Kong China	March 2005	Dissolved	14	0.34	0.26 -0.43	You et al. (2010)
		Particulate	14	0.172	0.085 - 0.27	
Singapore, Malaysia	November 2003 - March 2004	Unfiltered	40	--	0.045 - 1.8	Wurl and Obbard (2005)
Houston Channel, US	Summer 2002- Spring 2003	Filtered	209	2.7	--	Lakshmanan et al. (2010)
		Particulate	209	1.4	--	
		Total, as sum of separate dissolved and filtered	209	4	0.42- 62.9	
Delaware River, US	September 2001 - March 2003	--	--	--	1.9 - 6.2	--
Pearl River Estuary, China	May, October 2005, July, October 2006	Apparent dissolved	11	2363.8	0.018 0.007	Chen et al. (2011)
		Particulate	11	2665.8	0.02 - 14.7	

-- not analyzed or unknown

Puget Sound Case Study of PCBs

Similar to the copper case study, the goal of the PCB case study is to use the mass balance approach to ascertain the fate of PCBs released by unconstrained sources. PCBs from sealants of non-residential buildings constructed between 1945 and 1980 appear to be the major unconstrained source of PCBs to the Puget Sound basin. Volatilization of the PCB congeners with low extents of chlorination is a major release mechanism. However, the release rates are uncertain and there is no regional data to validate the extent of estimated releases. In addition, no quantifiable PCB concentrations in surface water were reported to Ecology by 2010 prior to the surface runoff study on of the Puget Sound Toxics Loading Analyses. Detection levels reported to Ecology ranged between 24 and 50 ng/L (Ecology, 2010).

Alternative methods for assessing PCB concentrations in storm and stream waters include estimating dissolved concentrations using semi-permeable membrane devices (SPMDs) and collecting large mass samples of samples by continuous-flow centrifuge or by large-volume filtration. Sandvik (2009 and 2010) deployed SPMDs in Washington freshwaters in 2007 and 2008, including at three locations in the Puget Sound area.

The highest estimated PCB concentrations for both years were found in the Spokane River, which is affected by the release of PCBs from a Superfund site. PCB estimated concentrations from deployments of SPMDs in the Duwamish River in Tukwila above the industrial area and in Lake Washington were higher than those deployed in the Snohomish River. All Puget Sound results ranked in the middle, between higher estimated concentrations from SPMDs deployed in the Spokane and Columbia Rivers and lower estimated concentrations from deployments in remote waters, such as the Queets and Walla Walla Rivers. Although the ranking of the Puget Sound deployments were qualitatively consistent with our general knowledge of PCB sources and pathway, the ranking among Puget Sound deployments could not be linked to a specific source.

No data on attenuation of PCBs in BMPs were found in the International Stormwater BMP database. In the Puget Sound region, Seattle Public Utilities and Herrera Environmental Consultants (2009) measured PCBs in street dirt, street sweepings and catch basin sediment (Table 3).

Concentrations of PCBs in street dirt (40-60 ug/kg) and catch basin sediments (34-150 ug/kg) collected from unswept area in the industrial area (Duwamish Diagonal) were similar to street dirt (19-29 ug/kg) and catch basin sediments (19-79 ug/kg) collected in the two residential areas. In contrast, PCB concentrations in street dirt (330 ug/kg), catch basin sediment (830 ug/kg) and sweeper waste (240 ug/kg) from streets routinely swept were much higher than unswept areas. Thus, it appears that the process of sweeping can itself mobilize PCBs. In the industrial areas of Seattle, PCB concentrations in dirt removed from catch basins of separate storm drain systems ranged between 19 and 600 ug/kg (City of Seattle, 2010).

Although not considered an urban stream, the actions associated with the lower Duwamish National Priority List site are illustrative of pathways of PCBs from industrial sources. SPMDs were deployed in the marine Duwamish Waterway adjacent to two combined sewer overflows

(Lower Duwamish Waterway Group, 2003) and the estimated PCB concentrations were as high as concentrations found in Portland Harbor Superfund Site. In comparison to the qualitatively consistent results with SPMDs, the extensive effort in measuring PCB concentrations on suspended solids in the source water for the Duwamish Waterway (Gries and Sloan, 2009) resulted in many qualified data values.

The PCB concentrations of sediments at the PACCAR site on the Lower Duwamish Waterway were above standards, but only 9 of 64 stormwater samples collected at the PACCAR National Priority List Site were slightly greater than the detection limit of 10 ng/L (Washington State Department of Ecology EIM database). Contamination of soils and groundwater, but not stormwater, was listed as concerns in the agreement order for the PACCAR site (Washington State Department of Ecology, 2008).

In 2005, solids in stormwater lines serving the Boeing Plant in the Duwamish industrial area were sampled for PCBs and a number of solid samples contained PCB concentrations exceeding 1,000 ug/kg. In 2005 and 2006, caulk from pavement and building slabs was sampled for PCBs and one sample of caulk from a building slab contained a PCB concentration of 40,500 mg/kg (Golder Associates, 2007). On September 29, 2010, Boeing Corporation signed an agreement with the U.S. Environmental Protection Agency (2010) to build a stormwater treatment facility at the site to reduce loadings of PCBs to the Lower Duwamish Waterway.

Review of Transport Mechanisms and Attenuation of PBDEs in Surface Waters

PBDEs are mainly volatized and abraded from commercial products into the air of residential and commercial spaces. Some abraded products are captured in dry sweeping and enter the solid waste stream. The gaseous PBDEs and fine aerial particles containing PBDEs are released to the natural environment through air-exchange to the building. PBDEs rinsed off fabrics in residential and commercial washing machine rinse water are transported to publicly owned treatment plants (Ecology and King County, 2011). Water treatment plants have been demonstrated to delivery substantial amounts of PBDEs to their receiving waters. In some areas of the developing world (e.g., Pearl River area, China), the importation and subsequent outdoor recycling of electronic wastes is thought to mobilize PBDEs in consumer electronic components (Guan et al., 2007).

As with PCBs, very little research has been conducted on the pathways and attenuation processes affecting PBDEs. The need for multi-media coordinated sampling plan for urban sources of PBDEs has long been known (Hites et al., 2004). No data on attenuation of PBDEs is available in the International Stormwater BMP database.

Mean PBDE concentrations in water (Table 11) collected from the urban settings of Paris (95,000 pg/L for 8 congeners), creeks in the San Francisco area (9,800 to 51,000 pg/L for 2 congeners), and Pearl River and its tributaries in China (8,900 pg/L for 17 congeners) are several orders of magnitude higher than concentrations found in the more rural areas of Lake Thun, Switzerland (53 pg/L for 7 congeners) or Lake Michigan (21 pg/L).

Mean PBDE concentration in estuarine waters collected near New York City (723 pg/L for 14 congeners) and Pearl River Estuary in China (900 pg/L) were higher than those collected from Hong Kong (33 ng/L for 8 congeners) and San Francisco (94 pg/L for 2 congeners). In estuaries, degradation in the sediments is thought to occur at a much faster rate than degradation in the water column (Oram et al., 2008) and relative importance of sedimentation and degradation differ among estuaries (Guan et al., 2009).

Table 11. Concentration of PBDEs in fresh, estuarine and marine surface water collected after 2000.

Location	Sample Dates	Fraction	Congener or number of congeners included in sum	Total PBDE (pg/L)		Reference
				Mean	Range	
Freshwaters						
Seine River	March - May 2008	Total	8	95000	--	Muresan et al. (2010)
Sacramento/ San Joaquin	2006	Total	BDE-47	100	100 - 400	Oram et al. (2008)
Guadalupe	2005	Total	BDE-47	8000	1700 - 26500	
Guadalupe	2005	Total	BDE-209	43000	8500 - 150000	
Coyote Creek	2005	Total	BDE-47	1800	900 - 3500	
Coyote Creek	2005	Total	BDE-209	8000	3400 - 22400	
Guadalupe	2006	Total	BDE-47	5300	600 - 18400	
Guadalupe	2006	Total	BDE-209	32300	1700 - 119000	
Eight riverine sources to Pearl River Estuary	March 2005 - February 2006	Dissolved	16	88	NA	Guan et al. (2009)
		Dissolved	BDE-209	425	nd - 1040	
		Particulate	16	466	NA	
		Particulate	BDE-209	5900	198-65000	
Lake Michigan	--	Dissolved	6	18	NA	Streets et al. (2006)
		Particulate	6	3.1	NA	
		Total	6	NA	NA	
Lake Thun, Switzerland	March, June, October, November, and December 2007	Particulate and Dissolved	7	52.6	NA	Bogdal et al. (2010)
River Aare, Switzerland	June and October 2007	Particulate and Dissolved	7	41.3	NA	
River Kander, Switzerland	June and October 2007	Particulate and Dissolved	7	61.5	NA	
Estuarine or Marine						
Pearl River Estuary, China	May, October 2005, July, October 2006	Apparent Dissolved	8	29.1	2.15 - 127	Chen et al. (2011)
		Particulate	8	26.1	6.2 - 79	
		Apparent Dissolved	BDE-209	118	nd - 537	
		Particulate	BDE-209	725	0.3 - 5690	
New York/New Jersey Harbor	Apr., Aug., Oct. 2000; Apr. 2001	Apparent Dissolved	14	96	NA	Zarnadze and Rodenburg (2008)
		Particulate	14	627	NA	
Hong Kong, China	March 2005	Apparent Dissolved	7	21	nd- 62	Wurl et al. (2006)
		Particulate	7	12	nd - 33	
		Apparent Dissolved	BDE-209	trace	NA	
		Particulate	BDE-209	nd	NA	
San Francisco Bay	2002 - 2006	Total	BDE-47	62	20 - 340	Oram et al. (2008)
	2002 - 2006	Total	BDE-209	32	10 - 530	
	2002	Total	22	--	0.2 - 293	Oros et al. (2005)

NA = not available
Nd = non detect
BDE = brominated diphenyl ether

Puget Sound Case Study of PBDEs

The PBDE case study is not comprehensive because very little PBDE environmental data were available for surface waters before the PSTLA. PBDE concentrations in water were assessed by measuring the accumulation of PBDE in SPMDs. SPMDs allow selective accumulation of the dissolved, readily bioaccumulative forms of organic compounds into the lipid component of the SPMDs.

SPMDs are unlikely to sequester PBDEs attached to particles. Except for congeners PBDE-47 and -99, most congeners were detected near the reporting limit. In 2005, Lake Washington ranked 3rd highest of four lakes or reservoirs in the amount of PBDE-47 accumulated in SPMD deployed and 4th highest of four lakes or reservoirs in the accumulated PBDE-99. Three of six SPMDs, including the one deployed in the Duwamish River, did not accumulate PBDE-47. Two of six SPMDs, including the one deployed in the Duwamish River, did not accumulate PBDE-99. In 2006, the Lake Washington SPMD accumulated both PBDE-47 and PBDE-99, and no other lake or reservoir SPMD was deployed.

Needs for Additional Data and Information

The literature review and environmental data for the Puget Sound basin available at the time of this addendum reveal significant gaps in our understanding of transport and attenuation mechanism of COCs in surface waters. The collection of COC data in surface waters from 16 small Puget Sound basins by Herrera Environmental Consultants, Inc. (2011) as part of the PSTLA provides an excellent opportunity to both further refine the Puget Sound release estimates and examine basin-specific attenuation process. The most immediate needs for data and information that would improve our understanding of the transport and attenuation process for the three COCs are listed below:

Copper

- The actual sales volume of copper-containing pesticides for residential gardens and lawns, copper for moss control and copper-containing, biocide-impregnated, asphalt roof shingles are needed.
- The percentage of copper in lawn and garden pesticides that escapes urban properties and is transported to surface waters, and the chemical form in which copper is transported, needs to be quantified.
- The concentrations of dissolved copper and copper on particles escaping from normal asphalt shingles and biocide-impregnated asphalt roof shingles in the Puget Sound region need to be quantified.
- The concentration of copper and antimony in brake pad and tire dust released from vehicles commonly used in the Puget Sound basin needs to be measured.
- The concentration of antimony on particles in roadway runoff needs to be measured to be used as a tracer of particulate brake pad dust in roadway runoff.
- The physical chemistry of copper (valance state) in brake pad dust needs to be investigated to model the geochemical processes that affect the retention of brake pad dust by commonly used BMPs.
- The concentration of copper in the various particle-size fractions needs to be quantified in roof particles, street dirt, sweeper waste, catch basin solids, inlets and outlets of BMP structures, and in urban streams to better predict attenuation in basin studies.
- The mass inventory of copper in the temporary reservoirs found in roadside grassy strips, drainage ditches and other stormwater infrastructures needs to be quantified to provide realistic estimates of the decrease in copper in urban streams once the use of copper in brake pads is discontinued.
- Better basin-specific data on the areas and type of roofs, the routing of roof runoff from urban properties, and the number and types in BMPs needs to be available as GIS layers.

PCBs

- The relative importance of electrical capacitors as compared to building caulk as primary sources of PCBs in commercial areas needs to be further investigated. These studies should include:
  - The prevalence of PCB-contaminated indoor and outdoor caulk present in non-residential buildings constructed in the Puget Sound basin between the 1950s to the 1970s needs to be quantified
  - Typical concentrations of PCBs in the primary sources (building caulk and electrical capacitors fluids) need to be determined.
- The prevalence of PCB-contaminated indoor and outdoor caulk present in non-residential buildings constructed in the Puget Sound basin between the 1950s to the 1970s needs to be quantified.
- Typical concentrations of PCBs in the primary sources (building caulk and electrical capacitors fluids) need to be determined.
- Atmospheric release rates of PCBs from building caulk and electrical capacitors need to be estimated.
- Methods for the quantification of PCBs in water samples need to be improved to lower the detection limit from ng/L levels to pg/L levels.
- Field sampling techniques, including the use of SPMDs and large-volume water filtration and/or centrifugation, need to be comparable, and standard methods for their use in sampling of PCBs needs development.
- The partitioning of PCBs between the dissolved phase and suspended particles in stormwater runoff and surface waters needs to be quantified.
- Selective surface water runoff sampling in the Puget Sound basin needs to be conducted using improved standardized methods in areas predicted to have elevated levels based on information gained regarding the density of PCB-containing buildings.

PBDEs

- The hypothesis that the primary pathway of PBDEs in Puget Sound urban surface water are from ventilation of residential and commercial indoor areas needs to be rigorously tested utilizing new data for surface waters (Herrera Environmental Consultants, Inc., 2011) and for air deposition (Brandenberger et al., 2010).
- New Puget Sound air and surface water PBDE data need to be synthesized together in the context of the physicochemical properties of individual PBDEs congeners to develop the next generation conceptual model of PBDE sources and attenuation in Puget Sound.
- A multi-media coordinated sampling plan for urban sources of PBDEs is needed. This data gap has long been known, and sampling should include monitoring of indoor and outdoor air, household products, atmospheric deposition rates and surface water concentrations. Hypotheses need to be developed to test the importance of the dominant sources and attenuation mechanisms affecting PBDE concentration in urban streams.

Summary

In the conceptual model of attenuation of contaminants of concern (COCs), the pathways that primary sources of COCs follow to Puget Sound were identified as surface runoff, combined sewer overflows, discharges from municipal and industrial wastewater treatment plants, atmospheric transport, direct releases to the marine waters, oceanic exchange and groundwater. The first step of the conceptual model was to categorize the primary sources described by Ecology (2011b) into groups that are transported by similar pathways, are affected by similar attenuation processes, and for which similar management actions apply.

Releases were grouped into two major categories by the extent to which the releases of COCs were initially constrained by physical infrastructures and the likelihood that the COCs enter the surface runoff pathway. Constrained releases are not likely to initially enter the surface water pathway and were not examined in detail. Unconstrained releases are released initially to the outdoor environment of Puget Sound and are likely to enter surface waters. Unconstrained releases were grouped into six categories based both on use and likely pathways to Puget Sound: 1) buildings and grounds, 2) roads and mobile sources, 3) land application as a liquid, 4) land application as a solid, 5) combustion from stationary sources and fugitive emissions, and 6) direct freshwater applications.

To test this conceptual model, case studies for copper, polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were conducted. The goal of a case study for a specific basin is to account for all the mass of the COCs released in the environment in permanent or temporary reservoirs in the basin that limit or delay the transport of the COC out of the basin through air and water pathways.

The availability of data on attenuation easily found in the literature and the availability of environmental data in the Puget Sound basin dictated the relative level of effort devoted to the case studies of copper, PCBs and PBDEs. The effort of this project was first limited to the surface runoff because other pathways were being examined in Puget Sound Toxics Loading Study. The majority of the effort for case studies was devoted to copper because of the availability of both attenuation data in the literature and environmental data in the Puget Sound model domain.

The copper case study focused on roof and road sources and examined literature studies on partitioning between particulate and aqueous phases and attenuation processes in segments along the surface water pathway. The pathways are discussed in this report under four headings: 1) *From Buildings to Roads or Stormwater Systems*, 2) *From Mobile/Roadway Sources to the Stormwater System*, 3) *From Stormwater to Urban Streams*, and 4) *In Urban Streams during Storm Events*. Literature studies indicate that the route that roof runoff follows off the property is highly site specific and attenuation of copper is controlled by the route roof runoff takes. Copper is highly attenuated in household infiltration fields in newer residential developments situated on highly permeable soils, while no attenuation occurs when roof runoff is piped directly to the street curb in older developments.

The fate of copper in vehicle wear material has been studied extensively. Up to 45% of the mass of brake pad dust was found to be nanoparticles (less than 0.1 um) suggesting that a large fraction of brake pad dust can be suspended in air and add to the regional air concentration. Additional copper accumulates on the vehicle itself and may be removed to sanitary sewers in commercial carwash facilities.

Two studies in Puget Sound are contradictory as to whether copper from vehicles accumulates on road surfaces. During a study of runoff from a bridge in Seattle, only about 3% of the estimated copper released by vehicles after two-day antecedent dry periods was collected in road runoff. Even more surprising, even less of the estimated copper release was captured in stormwater for a 15-day antecedent dry period, which suggests brake pad dust is more likely to be blown off the road as the road becomes drier. In this bridge study, the ratio of copper to antimony in the storm particles was very consistent, suggesting the antimony that is used as filler in brake pads may be useful as a tracer for the brake pad dust source.

While the small accumulation of copper in street dirt in a West Seattle neighborhood was similar to the results of the bridge study, dirt collected from Southeast Seattle streets accumulated more copper than was predicted from vehicles, suggesting another possible source of copper. Like roof runoff, the attenuation from vehicles is site specific. The copper in brake pad dust blown off the road is likely to be a temporary reservoir of copper along roads that can be mobilized during heavy rainfall.

Within both the stormwater system and urban streams, a number of BMPs can reduce loadings of total copper. The median short-term removal efficiency of 12 grassy biofilters ranged between 32% addition of total copper to 84% removal, with the width of the strip being an important controlling factor up to a width of 5 m. The removal efficiency of total copper in six retention and detention ponds ranged from 61% removal to 4% addition. In most cases, the removal of dissolved copper was much less than total copper, indicating that particle trapping is probably the major removal mechanism.

For the case studies, the estimated releases of copper from roof runoff and vehicle use in the Mill Creek in Kent and Auburn during three storms and Thornton Creek in Seattle and Shoreline during 32 storms was compared to calculated loadings. For both Mill and Thornton Creeks, only about 15% of the water that fell on the basin was transported to the mouth of the basin during the storm event based on the storm hydrograph. At most, 3% of the estimated total copper released in Mill Creek by vehicles and roofs was transported mostly as dissolved copper to the mouth of Mill Creek during a storm hydrograph. Only a small amount of this total copper was removed by street sweeping and catch basin cleanout programs.

From the literature review and geographical information on the basin, possible fates of the 97% of the total copper not transported to the mouth include infiltration into groundwater; trapping of particles by lawns, grassy roadside ditches, road shoulders and road right-of-ways; retention in the many structures installed in the basin; and settling of particles in vegetated channels of the creek in the 60% of the basin that is located in the low-gradient floodplain.

In Thornton Creek, up to 7% of the estimated total copper released was transported to the mouth of Thornton Creek during 31 of the 33 storm events (see equation 5), mostly as particulate copper. When the estimated release was adjusted downward to account for different braking patterns on the controlled access I-5, up to 28% of the estimated copper released into Thornton Creek may have transported from Thornton Creek during storm events. The greater proportion of the copper estimated to have been released that flows to the mouth of Thornton Creek relative to that in Mill Creek was probably a result of less efficient particle trapping within the Thornton Creek basin.

Less effective particle trapping in Thornton Creek was probably a result of a smaller proportion of the basin in the low-gradient floodplain, fewer BMP-related facilities, and heavy armoring of the banks of the lower Thornton Creek. Like the individual attenuation studies found in the literature, behavior of copper in the urban basins of Puget Sound is basin specific and modeling this behavior requires more information about roof runoff configurations, geography and stream habit than are available in standard land-use categories.

The state of the science for PCBs and PBDEs in water is quantification of ng/L and pg/L levels, respectively, and determining the partitioning between dissolved and particulate phases. Attenuation case studies are unavailable for even well funded monitoring programs. Little PCB data associated with loadings in urban streams is available in the literature and no actual studies on attenuation of PCBs in freshwaters could be located in the literature. In the absence of quantifiable PCB concentrations in urban stormwater and streams, a combination of SPMDs for qualitative interpretation of exposures coupled with analysis of PCB concentrations on solids seems to be an efficient initial screening tool to link PCB loads to Puget Sound to specific sources.

PBDEs in urban streams are thought to originate from dry and wet fallout after air exchange with indoor air contaminated with the vapors from furniture and other consumer products. However, the leaching of PBDEs from outdoor consumer products has not been examined in the Puget Sound region. A combination of SPMDs for qualitative interpretation of exposures coupled with quantitative analysis of solids seems to be an efficient screening tool for linking specific sources to loads to Puget Sound. An understanding of the attenuation process of PCBs and PBDE in urban settings will require separate analyses of the dissolved and particulate phases at sub-ng/L detection limits for PCBs and detection limits of 1 pg/L for PBDEs.

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Appendix A. Description of Basins

References cited in Appendices A, B, and C are listed in Appendix D.

Appendix A tables, A1 through A14, are linked to this report on the web as a zip file.

Mill Creek Basin

The Mill Creek basin is primarily in the City of Kent with a small portion located within Auburn that is south of S. 277th St. The Mill Creek basin has been divided into three sub-drainage areas (Golding, 2006; Anchor Environmental, L.L.C, 2008) based on land cover, topography and the stormwater infrastructure: Upper Mill Creek (7.3 km^2), 76th St. Outfall (2.8 km^2) and Lower Mill Creek (10.4 km^2). Approximately 47 km of roads in industrial areas and 29 km of residential roads are swept. Approximately 150 km of roads are curbed. The stormwater system of Mill Creek within the City of Kent (2010) superimposed on satellite imagery National Agriculture Imagery Program (2006) can be found at http://wa.water.usgs.gov/projects/linkingsources/data.htm.

Upper Mill Creek basin is located on the plateau above the Green River and is cut by a steep ravine containing the Upper Mill Creek. Upper Mill Creek basin is primarily newer residential housing (65% of the surface area), with the remainder being open space and a small, but increasing, portion of commercial facilities. Because of the newer construction and availability of open space in the southernmost part of the upper basin, the main branch of Upper Mill Creek and its tributaries that transverse housing developments contain a number of BMPs that detain water and retain COC including open vegetative channels, wetland ponds, and a large retention pond located at 108th Ave. S and S. 267th St.

The main stem of Upper Mill Creek flows from the retention pond down a steep ravine where additional stormwater in pipes is transported from residential areas to the east. Upper Mill Creek turns north one block east of East Valley Highway in an open channel and passes parkland before passing under East Valley Highway. In the short distance before passing under State Route 167, Upper Mill Creek passes through a detention pond and a large marsh area. Within several blocks of passing under State Route 167, Upper Mill Creek combines with the 76th St. outfall to form Lower Mill Creek.

The 76th St. outfall sub-drainage is mostly industrial (53 percent of area) and commercial including downtown Kent (23%) with equal portions of residential and open space (12%). The area of Mill Creek south of SR-167 and between two sets of train tracks is primarily piped with a few open segments near the ShoWater Center. Water is piped under SR-167, receives stormwater from an industrial area and discharges to Mill Creek along 76th Avenue.

Lower Mill Creek is primarily industrial (72%) including a remediated Superfund site on a former waste processing facility, a modern waste processing facility, a Boeing manufacturing plant, several large car lots, and numerous office and warehouse complexes. Lower Mill Creek is mainly open channel in ditches along 76th St. or open streambed, except where it is piped under five road segments. Lower Mill Creek along 76th St. is prone to flooding and when flow exceeds 180 cubic feet per second, water is diverted to the Green River Natural Resource Areas (Appendix D), and drained back to Mill Creek along SR-181 (West Valley Highway). Stormwater along much of SR-181, including stormwater from the Boeing Plant, is transported in vegetated channels, and flow is controlled by a vegetated weir near S. 204th St.

The area encompassed by S. 196th, S. 204th St., SR-181 and Green River is served by a large detention pond that is piped to Lower Mill Creek along SR-181. South of S. 204th St., Mill Creek is piped under SR-181 to the east where it flows through vegetative channels, past the Superfund site, under railroad tracks and a bike path along electrical transmission lines (location of USGS gage and Ecology sampling site), through a car lot and into a leveed channel overgrown with blackberry bushes until Lower Mill Creek discharges into Springbrook Creek just south of S. 180th St. Approximately 65% of the basin area was in the low-gradient lower flood plain of the Mill Creek basin. Recent long-term average flow was 0.30 m^3/s, which translates to a unit area runoff of 0.6 m.

GIS coverage of roof area for the Mill Creek basin is not available, so roof area coverages for the Lower Mill Creek and 76th Street Outfall sub-basins were created from satellite imagery (National Agriculture Imagery Program, 2006) and roof area in these two sub-basins (http://wa.water.usgs.gov/projects/linkingsources/data.htm) were summed (Table 7). Blocks of residential area in Lower Mill Creek and 76th Street Outfall sub-basins were sampled to obtain a 15% of roof area. This value was then applied to the residential area in the Upper Mill Creek sub-basins (USGS Table 6).

Thornton Creek Basin

An estimated 75,000 people live within Thornton Creek basin in the cities of Seattle and Shoreline. Data sources for the description of Thornton Creek basin (Appendix D) include: basin characterization reports by the Cities of Seattle and Shoreline, GIS coverages licensed from the City of Seattle superimposed on satellite imagery (National Agriculture Imagery Program, 2009, http://wa.water.usgs.gov/projects/linkingsources/data.htm). Stormwater schematics obtained from the City of Shoreline (2010) website and a visual inspection of the creek segments and significant infrastructures within Seattle and Shoreline by project personnel. Thirty miles of Seattle streets in Thornton Creek basin are swept and 180 tons of dirt per year are collected from Shoreline streets within Thornton Creek basin (Brian Landau, Surface Water and Environmental Services Program Manager, City of Shoreline, 2010).

The South Branch of Thornton Creek originates on the west side of I-5 in the vicinity of North Seattle Community College, where stormwater can enter wetland detention areas after passing through an oil/water separator. Three culverts/channels that pass under I-5 connect to a ditch on the west side of N.E. 1st Ave., in the vicinity of the Northgate Park and Ride lot. The parking lot of Northgate mall has been redesigned with vegetative mini-swales for water detention and pollutant retention.

Much of the water from I-5 and Northgate Mall is treated in an in-line system located under the Northgate Park and Ride. This treated water and the water passing under I-5 from North Seattle Community College passes through a new biofilter labeled the “Thornton Creek Water Quality

Channel” before passing under N.E. 5th Ave. East of N.E. 5th Ave., the South Branch of Thornton Creek flows northeasterly near 11th Ave. NE and NE 107th St. in a fairly low-gradient greenway that contains Northwest Park #6 that functions as an informal detention pond with fine-grained sediment. Northwest Park #6 is being improved by the community and receives stormwater piped from 5th Ave. N.E., NE Northgate Way, and Roosevelt Ave. NE, and from roadside ditches throughout most of the residential area. Towards the culvert under Roosevelt Way, the gradient steepens and the substrate is small- to medium-sized gravel.

Victory Creek joins the South Branch of Thornton Creek at NE 107th St. and flows southeasterly to Lake City Way through a steep ravine that is prone to flooding and erosion; much of the creek bank is reinforced with rip-rap and concrete. The lower part of this segment contains a number of park parcels collectively known as Thornton Creek Park #2, which contains small-meadow wetlands with fine-grained sediment. After joining Sacajawea Creek one block west of Lake City Way, the South Branch flows under Lake City Way through a culvert that is being remediated for fish passage.

The south branch is joined by Willow Creek on the east side of Lake City Way and several other tributaries before flowing northeast through the Ravenna/Blindheim Natural Area in a moderately wide, low-gradient channel that is prone erosion. Just west of Nathaniel Hale High School, the south branch joins Kramer Creek and flows east through the school campus and joins the north branch just east of N.E. 35th St.

The most western tributary of the North Branch begins near Meridian Park, which contains a small wetland (1.1 acres). The tributary is then piped about 20 blocks, along with stormwater from neighborhoods, to the main stormwater trunk at most arterial intersections. The water course daylights to an open channel east of Evergreen School, which has been recognized by the National Wildlife Federation for the construction of a wetland (4 acres) along Evergreen Creek that flows into Twin Ponds.

The main tributary of the North Branch begins as a piped reach that empties to Ronald Bog. Another reach begins as an open channel vegetated with blackberry bushes along the off ramp of I-5 to N. 175th St. that is piped to Ronald Bog. Ronald Bog is a 7.2-acre depression formed from the mining of peat and contains about 1 acre of wetland. From Ronald Bog, the North Branch is piped south and receives stormwater from a small residential area. Thornton Creek daylights between N. 170 and 167th St. and travels through private property in a open channel with a substrate consisting of fine-grained material before passing under N. 167th St. in a 5-ft culvert, where it is again piped through the Metro Bus Barn.

At the southeast corner of the bus barn property along the I-5 bus ramp, Thornton Creek discharges from a 4-foot pipe into a small wetland and then travels south in an open channel vegetated with blackberries, cattails and water parsley. North of N. 155th St. Thornton Creek enters a diversion structure, which diverts water to Twin Ponds when the flow exceeds 17 cubic feet per second based on a 1963 agreement between Washington State Department of Transportation and local property owners. The diversion occurs only during extreme rainfall. The diversion path to Twin Ponds contains open channels with both gravels and silt substrate and 2-ft culverts.

Twin Ponds were created from peat mining and are detention ponds since the southern outlet controls flow. Water flows from Twin Ponds to Peverly Pond through a mud-substrate channel that receives stormwater piped from about an eight-block residential and commercial area. Peverly Pond is a 1-2 acre wetland dominated by cattails. Water from Peverly reenters the main channel over a concrete sill.

Under normal Thornton Creek flows from the diversion structure along the west side of I-5 in an open channel that is heavily silted and vegetated with blackberry, veronica, cattail and water parsley. After receiving water from Twin Ponds and Peverly Pond, Thornton Creek enters a concrete-lined open water course with a silt substrate with some vegetation before passing under I-5 in a 1,500-ft-long, 6-foot culvert. From the culvert, the North Branch of Thornton Creek flows in a braided channel along 5th Ave. NE before entering Jackson Park Golf Course. Some of the water is diverted to an irrigation pond to satisfy Seattle's water right of 1.3 cfs that dates back to 1920. During summertime watering, about two-thirds of the flow of Thornton Creek is diverted.

From the golf course, Thornton Creek flows southeast through wooded area containing sand and gravel substrate and small wetland areas before passing under 10th Ave. NE. East of 10th Ave. NE, the creek passes through Thornton Creek Park #1 with a sand and gravel streambed and cuts through the lawn of a condominium complex before joining Littles Creek just east of 15th Ave. NE.

Littles Creek originates in Shoreline at a 0.5-acre, 8-foot detention pond at NE 170th St. and 15 Ave. NE. When the detention pond reaches capacity, stormwater is piped and channeled to NW 150th St. together with stormwater entering the main stormdrain from a commercial and residential area of about 280 blocks. Littles Creek daylights in grassy culverts and enters the open spaces of Paramount Park, which contain about 7 acres of wetlands, ponds and connected open channels with little armoring. Littles Creek receives stormwater from about 10 residential blocks before passing under NE 145th St. and into Seattle, where some of the water is diverted at high flow to a detention pond in Jackson Park Golf Course. Except for a small wooded segment in Jackson Park Golf Course, Littles Creek is piped to its confluence with the North Branch of Thornton Creek near NE 130th St.

From NE 130th St and 15th NE Ave, the North Branch of Thornton Creek flows southeasterly through pools created by check dams constructed in the backyards of residences. Besides reaching piped stormwater from the arterial 15th Ave NE, Hamlin Creek is said to discharge into the North Branch at 20th Ave. NE, just south of NE 130th (Thornton Creek Characterization Study). However, in Seattle GIS coverage, Hamlin Creek is shown only as roadside ditches and storm drains along 20th Ave. NE from NE 130th St. to the Seattle city line at 145th St. NE.

Hamlin Creek originates at NE 177th St. in Shoreline and receives stormwater from about 50 blocks of residential areas, which is piped to the northern border of Hamlin Park at NE 165th St. Hamline Creek is an open creek in Hamline Creek, but is intermittent most of the year because most of the water is lost to the sand soils within the park. Hamline Creek reemerges at NE 160th St. where it is immediately piped and reaches stormwater from large educational and commercial facilities before entering the ditches of 20th Ave. NE in Seattle.

After receiving piped stormwater from Hamline Creek, the gradient of the North Branch steepens as NE 125th St is approached. Through this segment, stormwater is delivered to the creek mainly by roadside ditches, but also receives stormwater from the arterial 125th NE St. From 125th NE St., the North Branch flows through the flat bottom ravine of Homewood Open Space, which contains several check dams and where erosion is evident, before passing under Lake City Way NE in a culvert that was being improved in August 2010. The North Branch of Thornton Creek continues southeasterly a short distance through backyards in steep rocky ravine where streamflow increase until reaching the confluence of Little Brook at NE 115 St. and 35th Ave. NE.

Little Brook receives stormwater from a small area on the southeast corner of Shoreline before being piped through single and multifamily residence areas and the commercial district of Lake City. Little Brook discharges to a vegetated 11-acre detention pond constructed in 1997 that can detain one acre-foot volume of stormwater. From the detention pond, Little Brook flows through backyards in a steep ravine, with banks overgrown with vegetation and some concrete channels. Stormwater in this high-density residential area is carried to Little Brook in roadside ditches.

From the confluence with Little Brook, the North Branch flows southerly for eight blocks in the floodplain in a high armored segment with check dams and signs of erosion, then joins the South Branch just east of 35th Ave. NE across from the Nathaniel Hale High School. Downstream of the confluence, the Main Branch of Thornton Creek flows adjacent to and through the Meadowbrook Detention Pond constructed in 1996 to hold up to 16 acre feet of water. During severe storms, water is diverted directly to Lake Washington from a bypass pipe located in the pond. Downstream of the pond, the Main Branch flows through highly armored open channels. The streambed is rocky with deposits of silt during the summer. Mock Creek and an unnamed tributary, which receive stormwater from roadside ditches and storm drains, enter the Main Branch between the detention pond and the crossing at NE 95th St.

From NE 95th St., the main branch of Thornton Creek drains 2.3 km^2, including the Sand Point Natural Area, and passes under Sand Point Way NE. The Main Branch is heavily armored until entering Matthews Beach Park. From the slope of Wedgewood plateau, Matthews Beach Creek flows mainly in pipes and ditches through housing developments on the slope and only flows in an open channel near the base of the slope before joining the main branch within a short distance of Lake Washington. Maple Creek also flows from the Wedgewood plateau partially in pipes and joins the main branch adjacent to the parking lot of Matthews Beach Park.

Appendix B. Methods for Road Releases

Mill Creek Basin

Total daily miles traveled in basin

For a particular segment of road, the average daily vehicle miles traveled (ADVMT) is equal to the average daily traffic (ADT) multiplied by the length of the road segment. ADT is the average daily traffic measured by an air pulse in the condensed tube converted to an electric signal when a vehicle drives over the devise. Kent arterial average weekday traffic (AWDT) data was obtained for March of 2006 (Appendix D). The road segments were manually digitized using ArcGIS and geometric calculations from data in the GIS attribute table.

The average weekday traffic flow was adjusted using the 0.933ADT/AWDT factor determined from an extensive data set of Seattle arterials that provided both ADT and AWDT. The assumption is that weekday to weekend traffic patterns are similar between Seattle and Kent. Since Mill Creek basin is 44% industrial, Thornton Creek basin is primarily residential and the traffic count declines more noticeably in industrial areas on weekends, 0.933ADT/AWDT likely overestimates the average daily traffic flow. The summary of road segments location, length, and AWDT are shown in Table A9. The ADVMT for the basin is the sum of all ADVMT for arterial and controlled-access roads segments within the basin. The following assumptions were made:

1) Traffic volumes are homogeneous throughout the length of the road segment.

2) Traffic patterns in the study are relatively unchanged from one year to the next within the period of interest.

Average daily traffic data for Kent control access roads were obtained from the Washington State Department of Transportation (Appendix D). These ADT measurements were available for the study sample year 2005. Approximately 1.4 miles of Interstate-167 was the only control access road within the Mill Creek basin and contributed to 27% of the total ADVMT.

The ADVMT in the Mill Creek basin were 424,100 miles on arterials and 153,380 miles on controlled access roads (Table 6). The following observations introduce errors into this calculation:

1) Many less traveled residential roads are not included in this project, resulting in an underestimate in brake pad and tire material accumulation.

2) Traffic volumes are not homogeneous; cars enter and exit the segment at unmonitored locations.

3) Traffic volumes do change from one year to the next and from one month to the next (Sharma et al., 1996).

Determination of antecedent dry period

Hourly precipitation data for Seattle-Tacoma International Airport (SEATAC), which is located about 3 km from the edge of the basin (National Oceanic and Atmospheric Administration, National Weather Service, Appendix D) and daily precipitation from Sequoia JR/High School and Panther Creek (King County Hydrologic Monitoring Program are in Appendix D. The total precipitation amounts (in cm) during the three 2-day storms were calculated for the three stations (Table A8). In addition, the maximum hourly rates (cm/hr) observed at SEATAC are also presented Table A14.

A threshold amount of precipitation needs to be defined in order to calculate the antecedent dry period. The minimum value of rainfall recorded at the SEATAC weather station is 0.01 inch. On days of light rain when no, trace, or 0.01 inch fell in each of the 24 hourly measurements at SEATAC, the daily rainfall was generally around 0.13 cm (0.05 inch), which was used as definition of threshold rainfall. The antecedent dry period averages from 11 to 17 days and was generally similar among precipitation stations, except that antecedent dry period derived for Panther Creek for the September 2005 storm was six days longer than the antecedent dry period for SEATAC and Sequoia Junior High School.

Golding (2006) used a rainfall threshold of 0.26 cm (or 0.10 inch), which corresponded to the lowest rainfall resulting in an increase in flow in Mill Creek. The August 2005 storm was most affected by the definition of threshold rainfall increasing from 11 days for a daily threshold of 0.13 cm to 37 days for a threshold of 0.26 cm.

Road source event releases

The copper released to roads that is available for transport by Mill Creek during the three events is as follows:

Copper release (mg) =ADVMT * Unit vehicle release * Duration of release (eq B1)

where ADVMT is the average daily vehicle miles traveled listed in Table A7, the unit vehicle release is taken as 1.02 milligrams of copper per vehicle mile, consistent with the release of Robert et al. (2011):

Duration of release (days) = length of antecedent dry period + days of storm -1 (eq B2)

The minus one day is to account for averaging when using data with the resolution of one day. For instance, if sufficient rain fell on day 1 to initiate the antecedent dry period, and no rain fell on day 2, and the storm occurred during day 3 and 4, the antecedent dry period is one day and the storm length is 2 days. The previous storm could have ended anytime during the 24 hours between sampling times on day 1 and the storm could have ceased in the latter part of the measurement period of day 4.

Based on the Unit Vehicle release used to calculate total releases of copper from vehicles within the Puget sound, between 15,357 and 23,035 grams per storm event were estimated to have been released within the Mill Creek basin if 0.13 cm/d is sufficient to wash copper off roads (lower threshold rainfall) and between 23,035 and 48,630 if at least 0.26 cm/d is required to wash copper off roadways (Table 8). Since the SR-520 study suggests that release from controlled access highways is less than arterials because of braking pads, we developed a release alternative algorithm for event release:

Copper release =[($ADVMT_{ca}$ * UVR_{ca}) + ($ADVMT_{ar}$ * UVR_{ar}]* Duration of release (eq B3)

where $ADVMT_{ca}$ and $ADVMT_{ar}$ are the ADVMT for controlled access and arterials (Table A9) and UVR_{ca} and UVR_{ar} are Unit vehicle releases for controlled access (0.03 mg/VMT from 520 Study) and arterials (0.59 gm/VMT from San Francisco (Rosselot, 2006). Using these alterative unit vehicle releases, the event total copper release was estimated to have been between 3,058 and 4,587 grams for the lower rainfall threshold and between 4,857 and 9,664 grams for the higher rainfall threshold.

Thornton Creek Basin

Total daily miles traveled in basin

Seattle arterial ADT data were available with an intersection providing the street names and the direction of traffic flow (Prince, 2010). Two nearby intersections were identified and all measurements between intersections were summed. For example, the ADT for the condensed tube located at Meridian Ave N and 145th St heading south was coupled with ADT from the condensed tube between Meridian Ave N and 130th St heading north. The averages for each direction were added together, resulting in the total ADT. In some cases, where the traffic in both directions was similar, the average of all segments was doubled to get the total ADT on the road segment.

The length of the segment was determined in the same manner as with the Kent traffic data, by digitizing in ArcGIS and calculating the geometry in the attributes table. We assumed that any measurement of zero was made in error and therefore were not considered in any of the calculations. Seattle arterial ADT and AWDT were available for the years 2000-2009 (Table A9).

Shoreline arterial AWDT was available in map form (Appendix D) and therefore easy to digitize in ArcGIS to find the respective road segment lengths (Table A9). The years 2005-2009 were averaged and the same 0.933ADT/AWDT factor used to convert Kent AWDT to ADT was used here (Table A9).

Controlled access in Thornton Creek was limited to about 4.5 miles of Interstate-5, from 89th St to 175th St and accounted for 65% of the total calculated VMT (Table A14). The average daily traffic volume from 2006, 2007, 2008, and 2009 were averaged. The total vehicular miles traveled on arterials and control access roads within the Thornton Creek basin per day were 478,442 and 893,399, respectively (Table 6).

Determination of antecedent dry period

Hourly precipitation data from Boeing Creek and Brugger Bog North King County from the King County Hydrologic Monitoring Program (2010), and partial records from and Haller Lake (1998-2008) and Green Lake (2006, 2007 and 2009) from the King County Lakes Stewardship Program (2010) were statistically averaged to determine the total rainfall per storm event. Since Seattle-Tacoma International Airport from National Weather Service/NOAA is distant from the Thornton Creek basin, data on daily precipitation, event rainfall, antecedent dry periods and maximum hourly rainfall from SEATAC are given for information purposes and were not used in the load calculations for Thornton Creek. The storm events were divided into five categories based on the duration of the storm and the antecedent dry period derived from the rainfall data.

For the antecedent dry period under the two storm threshold for rainfall, the antecedent derived from the two to four precipitation stations in north King County were more variable than the three stations in Kent. In some cases, there were discrepancies among data from different stations, probably originating from differences in time of day that the daily precipitation measurements were made for the two programs. The percent difference of antecedent dry period under the definition of threshold rainfall was greater for shorter antecedent storms than for longer antecedent dry periods. Two storms (September 18, 1998, and August 11, 2009) had antecedent dry periods greater than one month.

Road source event releases

Within a given basin, estimated road releases are dependent on the average daily vehicle miles traveled, the Unit Vehicle Release and the antecedent dry period. Based on the Unit Vehicle Release of 1.02 mg/VMT used for calculating Puget Sound releases, the estimated release of total copper during the 32 storm events ranged between 3,040 and 113,500 grams. When the alternative lower Unit Vehicle Release described for Mill Creek that takes into consideration differing braking patterns on controlled access roads, the estimated release of total copper during the 32 storm events decreased by an order of magnitude and ranged between 309 grams and 11,500 grams.

Appendix C. Methods for Roof Releases

Mill Creek Basin

Roof area

Since copper release from roofs is specific to land use, the fraction of roof area to area by land cover type (Table 6) is needed to calculate the roof releases and needed to be estimated by sampling with ArcGIS. Two or three square blocks were randomly selected per cover type, except Forest/Field where the margin of error in sampling was unacceptable, and the Ecology estimate of 0.005 was used instead. The roof area was digitized from satellite imagery in ArcGIS and geometry calculations were performed in the attribute tables. Three residential areas were sampled with an average rooftop fraction of 0.15.

One sample of commercial area yielded a ratio of 0.24 for roof area to surface areas. However, the industrial area sample of 21% was used since 83% of the commercial/industrial land cover type is industrial (Golding, 2006) and was considered a better estimate of the rooftop fraction. The roof areas, $(Area)_{SA,LC}$, for forest/fields, commercial/industrial and residential in the Mill Creek basin are given in Table 6. The discrepancy between the total roof area in Table 6 and Table 7 is a result of estimating different parameters in the two methods.

Event rainfall

The average total rainfall collected over the 2-day storm at SEATAC, Sequoia JR/High School, and Panther Creek (Table A8) were averaged and ranged between 0.73 cm and 1.08 cm (USGS Table 7), with relative standard deviations ranging from 25% to 38%.

Roof source event releases

The weighted average of the copper concentration in roof runoff from different types of roof material within land use is given as:

$$(TCu)_{LC} = \sum((\text{Roof type}_{(1,2..n)}\ \text{frx})_{LC} * (TCu)_{RT}) \qquad \text{(eq. C1),}$$

where $(\text{Rooftop frx})_{LC}$ is a fraction of a specific rooftop type for the specific land cover and $(TCu)_{RT}$ is average total copper concentration per roof type (ug/L). Applying the $(TCu)_{RT}$ for the different rooftops to the distribution of rooftops for a give land use $(\text{Rooftop frx})_{LC}$, the $(TCu)_{LC}$ can be calculated for each land use and is given in Table 7. Total copper releases for roofs are calculated as:

$$\text{Roof release (g)} = (\text{Area})_{\text{Mill Creek},LC}\ (\text{km2}) * (TCu)_{LC}\ (\text{ug/L}) * \text{rainfall (cm)} * (10^6\ m^2/km^2) * 1m/100\ cm * 1000\ L/m^3 * 10^{-6}\ \mu g/g) \qquad \text{(eq. C2).}$$

The release of copper from roofs in the Mill Creek basin during the three 2005 storms is dependent only on the rainfall since $(\text{Area})_{\text{Mill Creek,LC}}$ and $(\text{TCu})_{\text{LC}}$ do not vary. Copper release varied between 1,648 and 2,415 grams per the three storms (Table 8). These calculations are predicated on the assumption that copper releases for roof types commonly found in the Puget Sound region are proportional to rainfall (constant copper concentration that is independent of rainfall). In contrast, Zobrist (2000) and Bucheli et al., (1998) observed that the concentrations of metals and organics decrease after 1 mm of rainfall. Thus, it is likely that these releases overestimate the actual releases for rainfall events over 1 mm.

Thornton Creek Basin

Roof area

Roof area coverage per land cover type was determined in the same manner as in the Mill Creek basin, by randomly selecting representative samples, except that the digitized roof layer was provided by the City of Seattle. Three residential areas and two commercial areas were selected and the averages used were 17 and 25%, respectively. Land cover fractions of 0.14 (Forest/Field/Other), 0.12 (Commercial/Industrial) and 0.74 (Residential) were taken from Thornton Creek Watershed Management Committee, City of Seattle (2000). The fractions of roof area for a specific land cover were applied to the three land cover types to obtain the total rooftop area for each land cover (Table 7).

Event rainfall

Total rainfall among the three to four precipitation stations were generally within 50%. Rainfall for storms of short duration (1-2 days) ranged from 0.66 to 4.07 cm. In contrast, the total rainfall for the 7-day storm in November 2006 that flooded I-5 was 14.64 cm.

Roof source event releases

The basin area times the total rainfall is the runoff volume. Runoff volume per event multiplied by copper concentration for each roof volume for each land cover and unit conversion factor gives the roof loading in grams of total copper. The estimated release of copper from roofs is directly proportional to total event rainfall for each basin and ranged between 385 and 24,883 grams.

Appendix D. Data Sources of Appendices

Appendix A: Description of Basins

Mill Creek

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Appendix B: Methods for Road Releases

Total daily miles traveled in basin

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Appendix C: Methods for Roof Releases

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